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Investigations into the Mechanism of
the Photodechlorination of
Pentachlorobenzene

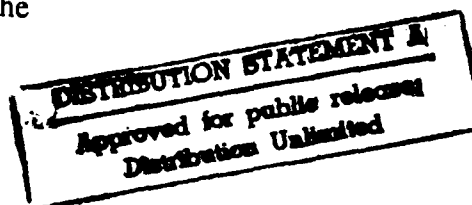
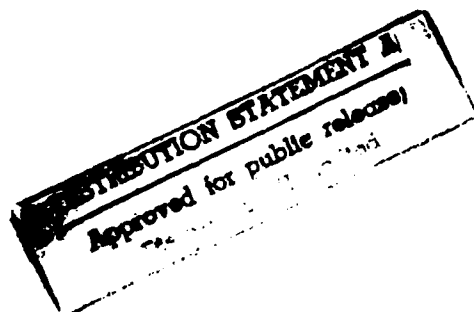
by
Robert Dean Schmidt

A THESIS
submitted to
Oregon State University

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in partial fulfillment of
the requirements for the
degree of

Master of Science



Completed May 31, 1991

Commencement June 1992

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APPROVED:

P. K. Freeman

Professor of Chemistry in Charge of Major

Carol W. L. H.

Head of Department of Chemistry

John C. Ringle

Dean of the Graduate School

Date thesis is presented: May 31, 1991

Typed by: Robert Dean Schmidt

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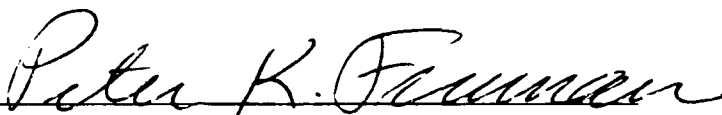
*Dedicated to the memory of my father,
Nikolaus Schmidt*

AN ABSTRACT OF THE THESIS OF

Robert Dean Schmidt for the degree of Master of Science in Chemistry presented on May 31, 1991.

Title: Investigations into the Mechanism of the Photodechlorination of Pentachlorobenzene.

Abstract approved: _____




Peter K. Freeman

Several experiments were undertaken to investigate the mechanism of photodechlorination of pentachlorobenzene. The thermal methoxydechlorination reaction of pentachlorobenzene was studied. In DMSO at 50 °C sodium methoxide reacts smoothly with pentachlorobenzene to give three tetrachloroanisole isomers. A second-order kinetic plot for this reaction is linear to high precision, indicating that the reaction is second order overall. The rate of the reaction and the product regioisomer distribution are not affected by the presence of radical traps such as galvinoxyl, by reaction in the absence of oxygen or by benzyne intermediate traps such as 1,3-diphenylisobenzofuran. The rate of the reaction is reduced linearly as the starting mixture is diluted with methanol. These facts suggest that the reaction follows the classical S_NAr mechanism.

The proposed structure of the pentachlorobenzene radical anion formed by photolysis in the presence of triethylamine is analogous to the σ -complex intermediate in the S_NAr reaction. The regiochemistry of these two types of dechlorination was compared and showed a fair correlation. The differences in

regiochemistry were attributed to steric effects between the nucleophile and the aromatic *ortho* chlorine atoms in the S_NAr reaction.

Tetrachlorophenyl radicals were generated by thermal decomposition of 1,2,4,5-tetrachlorobenzeneazotriphenylmethane in the presence of CCl_4 and a hydrogen atom donor. The selectivities of chlorine versus hydrogen or deuterium atom abstraction were determined in several systems and applied to selectivity of atom abstraction observed in photochemical experiments. The results support the hypothesis that, in the photolysis of pentachlorobenzene in the presence of triethylamine, the intermediate tetrachlorophenyl radical exists as an unencumbered free radical rather than in a solvent caged pair with triethylamine.

It was anticipated that the rate of photodechlorination would increase in micellar solutions if triethylamine was added. Experiments showed no such expected increase in rate, and showed regiochemistry similar to that of the same reaction in the absence of triethylamine. 

ACKNOWLEDGEMENTS

There are many people without whose help this work might not have been finished and to whom I owe my sincerest gratitude. I am grateful to my mentor, Dr. Peter K. Freeman, whose patient guidance and wise counsel made the work interesting, enjoyable and fruitful. Many thanks are also due to Dr. Gerald J. Gleicher, whose suggestions (and historical anecdotes) often made the work easier.

Quite a few of my colleagues donated freely of their expertise and time to help me set up and conduct experiments, and much of the success of this work I owe to them. Drs. Gary "Big Toe" (alternately, "The Skipper") Clapp, Belaid "Chief" Mahiou and Ramnath N. Iyer imparted much practical wisdom. Eric Carlson, Donald Griffin and Brian Arbogast ran some excellent short-notice spectra for me which were crucial to several experiments.

There was also indispensable help from outside the lab, and heaps of gratitude are due:

- to my mother, who taught me the importance of hard work and the lasting value of formal education.

- to the doctors at Madigan Army Hospital, Tacoma, for restoring me to working condition.

- to my daughters, Anna and Kristina, for making sure I never left for school without a kiss and a hug.

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Finally, I would like to thank the U.S. Naval Postgraduate School Civilian Institutions Program and the Naval Sea Systems Command for funding and sponsorship.

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Investigations into the Mechanism of the
Photodechlorination of Pentachlorobenzene.

INTRODUCTION

Photochemical Background.

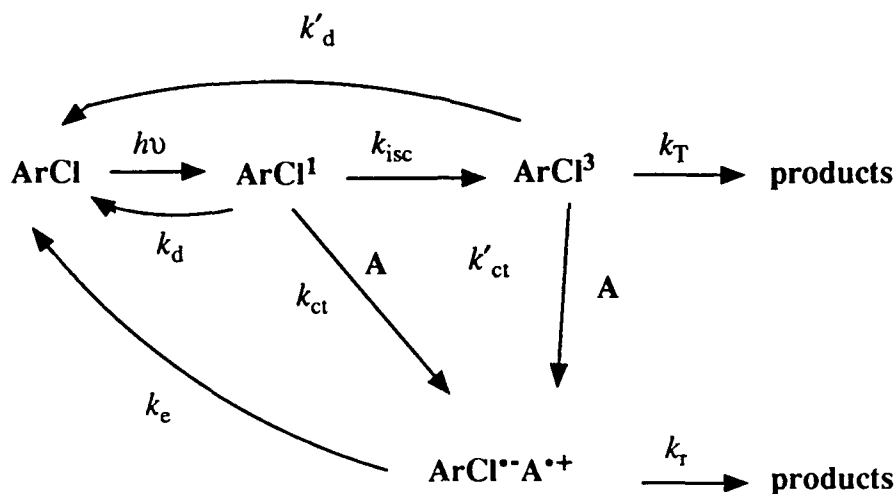
Many polychlorinated aromatic compounds are known to be environmental pollutants. Perhaps the most notorious of these are the polychlorodibenzodioxins and polychlorobiphenyls (PCB), although there are many other compounds in this class which have been detected in environmental samples and which can adversely affect living organisms. For example, chlorinated benzenes have found extensive industrial, commercial and agricultural applications¹ and have been detected in inland and coastal waters,² soil³ and municipal waste incinerator fly ash.^{4,5}

Environmental chlorinated benzenes are introduced by "direct" sources such as toxic waste dumping and industrial effluents, and "indirect" sources, for example, the incineration of toluene or chlorophenols in the presence of hydrochloric acid.^{4,5}

Chlorinated benzenes have been found in animal tissues, and the toxicology of these compounds has been the subject of extensive scrutiny. In aquatic animals, it has been found that the toxicity of these compounds increases with increasing chlorine substitution. In studies with the guppy (*Poecilia reticulata*), the acute toxicity (LC₅₀) was found to decrease (that is, the agent becomes more toxic) steadily by almost three orders of magnitude in going from monochlorobenzene to pentachlorobenzene.⁶ Studies on zebra fish (*Brachydanio rerio*) showed adverse effects of chlorobenzenes on survival, embryo-hatchability and growth.⁷

It has been observed that chlorobenzenes can be dechlorinated by exposure to ultraviolet light. Knowledge of the photochemistry of these compounds is of current interest, primarily in order to attain a better understanding of how they are degraded in the environment and how they can be dechlorinated to less toxic forms. In the presence of electron donors such as triethylamine, polychlorobenzenes exhibit enhanced photodechlorination.⁸⁻¹⁰ This observation suggests a potentially powerful tool for the detoxification of these pollutants.

The mechanism of photodechlorination of pentachlorobenzene in the presence and absence of triethylamine has been the subject of much investigation in this laboratory. As mentioned before, the presence of an electron donor increases the rate of dechlorination. Interestingly, the product distribution is also altered by the presence of triethylamine, which suggests a change in mechanism. The proposed mechanism (Scheme I) involves formation of an excited singlet state

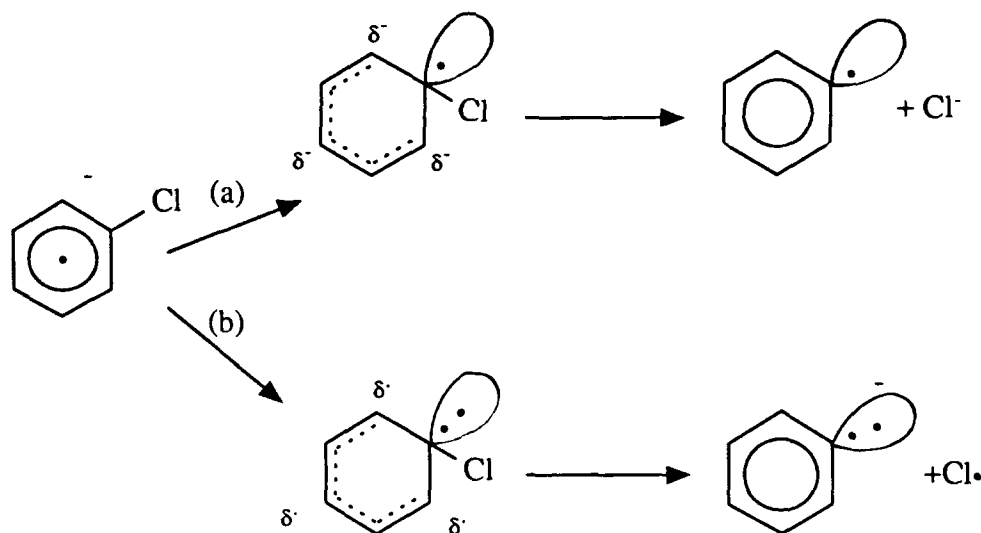


Scheme I

which has sufficient energy to directly undergo carbon-chlorine bond homolysis. However, since the efficiency of intersystem crossing to the triplet state is high (0.4 - 1.0 in cyclohexane),¹¹ and since electron transfer from the donor is fast, this singlet bond fission is generally not observed, and the formation of dechlorinated products arises from the radical anion/excimer.⁹

By itself, the triplet state does not normally have sufficient energy to undergo C-Cl bond homolysis, but there are two ways it can still achieve this.^{8,9} First, it can form an exciplex with the electron donor. Second, it can form a charge-transfer excimer with a ground state molecule of chloroarene. In both cases, the arene radical anion is formed (although probably only a small degree of charge transfer is involved in the excimer), and this can lose chlorine by one of two pathways (Scheme II), one (a) which results in a phenyl radical and another (b)

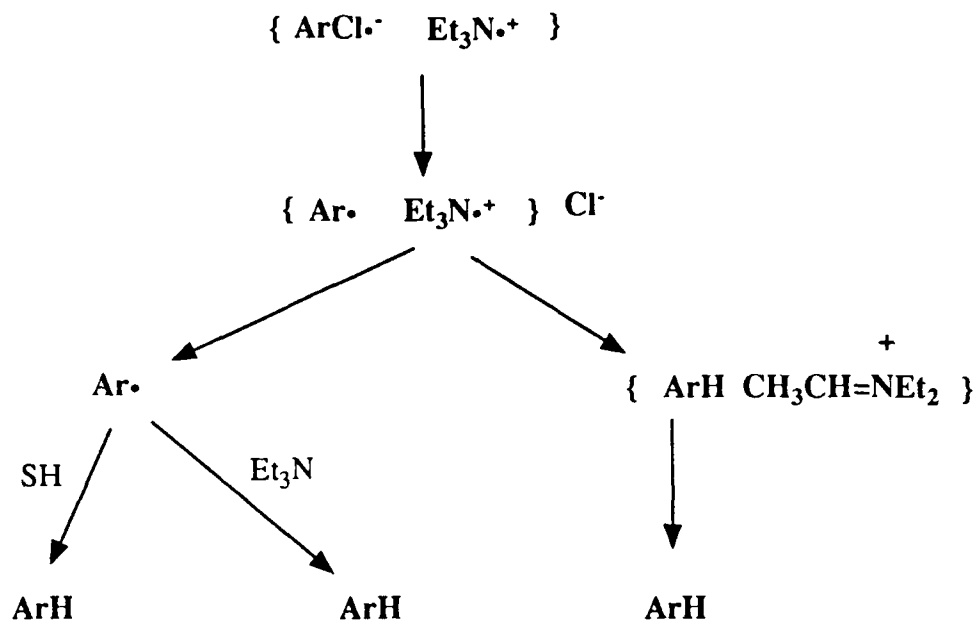
which results in an aryl carbanion. It has been proposed,⁹ based on the



Scheme II

regiochemistry of products formed from this reaction, that path (a) is the predominant path. The transition state which controls this bond fission pathway is analogous to the σ -complex intermediate in nucleophilic aromatic substitutions in that it has an sp^3 -like center and a delocalized negative charge on the ring much.

When the phenyl radical is produced, it is still associated with the amine radical cation. It can conceivably abstract a hydrogen atom exclusively from the associated amine, or it can diffuse away to abstract a hydrogen atom from any source in solution (Scheme III). One study³⁶ which has attempted to determine the



Scheme III

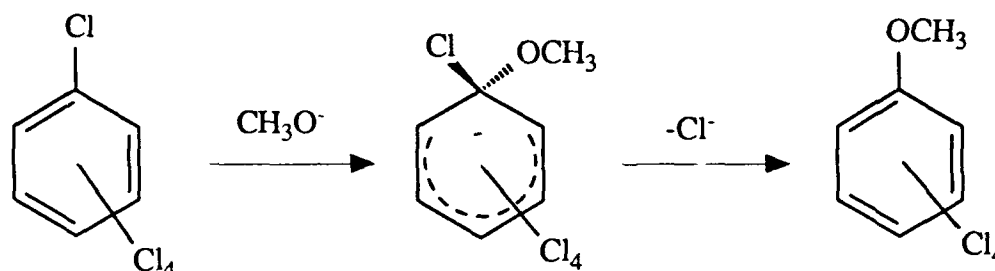
correct pathway for hydrogen atom abstraction used deuterated acetonitrile as a solvent, so that deuterated arene should be present if the free phenyl radical pathway is occurring. However, the results of this investigation were not clear.

Another aspect of this reaction which has been studied^{12,13} is the behavior of an isolated chloroarene radical anion. Spatial isolation of the arene from the electron donor can be achieved by dissolving pentachlorobenzene in an aqueous micellar solution such as 0.200 M cetyltrimethylammonium bromide (CTAB). The pentachlorobenzene is contained inside the spherical micelle, and the triethylamine is kept outside the micelle where it exerts its electron-donating ability from a distance. Oxygen quenches the radical anion back to the ground state, so experiments have been done in the absence of air.¹³ However, since at

low solute concentrations the probability that oxygen will occupy a micelle already occupied by a chloroarene molecule is very low, the presence of oxygen in solution should not inhibit the rate of photodechlorination. The reaction rate has been measured in the absence of Et_3N ,¹⁴ but this has yet to be done in the presence of Et_3N . If the reaction can be made to proceed efficiently with Et_3N in oxygenated aqueous solution, then a convenient method for toxic waste disposal could be developed.

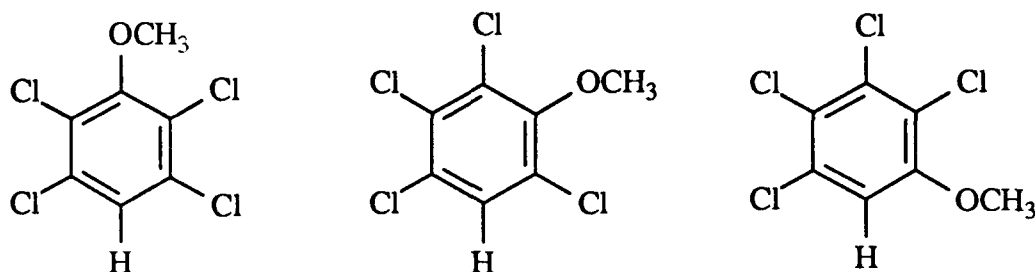
Methoxydechlorination of Polychlorobenzenes.

As discussed above, the likely pathway for loss of chlorine from the pentachlorobenzene radical anion is one which results in a tetrachlorophenyl radical and proceeds *via* a σ -complex-like transition state. The regiochemistry expected in the products formed by this mechanism has been predicted by Freeman et al.,⁹ based on work by Chambers et al.,¹⁴ and experimental product distributions were in excellent agreement with these predictions. Since the transition state in the proposed mechanism resembles that in a nucleophilic aromatic substitution, it might be expected that substitution of a single chloride by a nucleophile in pentachlorobenzene should give a similar product distribution *if* the substitution followed the conventional $\text{S}_{\text{N}}\text{Ar}$ mechanism (Scheme IV).



Scheme IV

In this work, such a study was conducted using methoxide ion as the nucleophile. This reaction has been reported by several groups.¹⁵⁻¹⁷ Holleman¹⁵ reported the reaction of pentachlorobenzene with sodium methoxide in methanol under quite harsh conditions (180 °C for 7.5 hours). Under these conditions, only 2 products, 2,3,4,5- and 2,3,5,6-tetrachlorophenol, were detected. It was later reported¹⁸ that much milder conditions could be used to methoxydechlorinate hexachlorobenzene if pyridine were used as the solvent. This observation was applied to pentachlorobenzene by Yakobson et al.,¹⁶ who found the product distribution shown in Figure 1 (pyridine 110 °C, 1 hr, 2:1 methoxide/pentachlorobenzene). A small amount of two tetrachlorophenols (*para*



Tetrachloroanisole Isomers:

2,3,5,6 (" <i>para</i> ")	2,3,4,6 (" <i>meta</i> ")	2,3,4,5 (" <i>ortho</i> ")
50-52%	7-9%	33-38%

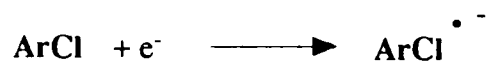
Figure 1. Product Percentages from Pentachlorobenzene Methoxydechlorination Reported by Yakobson, et al.¹⁶

and *meta*) was also isolated. The products were analyzed by GC. The *para* and *meta* isomers were found to be unresolvable by GC, so differential infrared spectrophotometry was used to determine their concentrations. A more rapid reaction under even milder conditions was reported in dimethylsulfoxide (DMSO) by Bolton et al.¹⁷ In a 9:1 v/v solution of DMSO:methanol at 50 °C, a rate constant of 0.14 M⁻¹sec⁻¹ was reported.

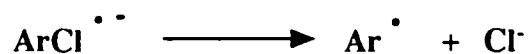
It has been assumed that substitution reactions like the above example proceed *via* the so-called S_NAr (addition-elimination) mechanism (Scheme IV).¹⁹ However, an alternate mechanism which may occur under certain conditions and mimic the results of the S_NAr mechanism was proposed by Bunnett.^{20,21} This mechanism involves radical species and is therefore named S_{RN}1 (for

substitution, radical nucleophilic, unimolecular). In the case of pentachlorobenzene, an $S_{RN}1$ mechanism would be as shown in Scheme V.

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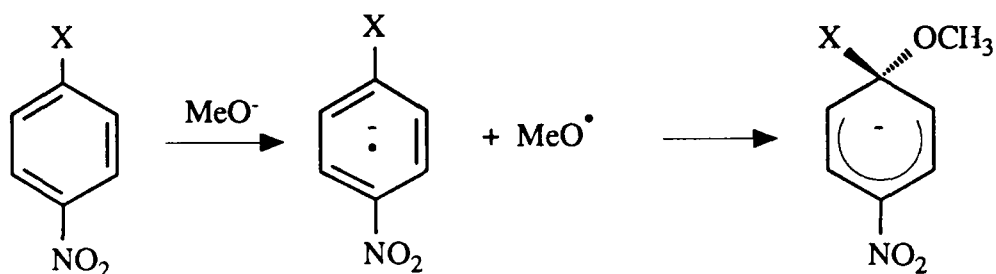


PROPAGATION:



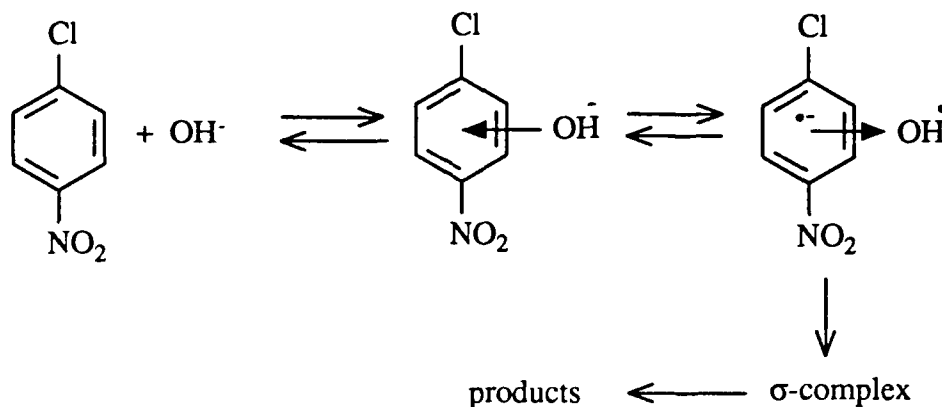
Scheme V

Another radical mechanism which has been proposed for nucleophilic aromatic substitution differs from the $S_{RN}1$ mechanism in that it does not involve a radical chain. Shein et al.²⁴ have produced evidence for a single electron transfer (SET) mechanism in which transfer of an electron from methoxide to the arene preceeds formation of a σ -complex (Scheme VI). Indeed, studies on bimolecular



Scheme VI

aliphatic nucleophilic substitution (S_N2) processes have turned up evidence for an SET mechanism there as well.^{23,24} More recently, Bunton²⁵ has presented evidence which supports this aromatic SET mechanism but which proceeds *via* a π -complex in equilibrium with a charge transfer complex instead of the free radical anion and methoxide radical (Scheme VII).



Scheme VII

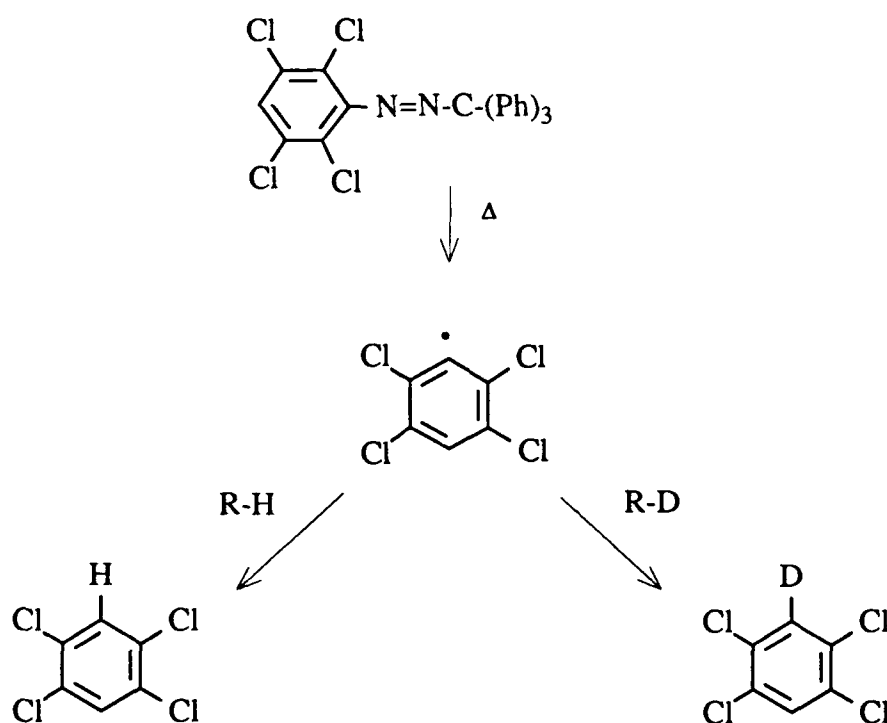
One goal of this work was to investigate this reaction to see which of the above mechanisms best fit. Since the proposed photochemical intermediate resembles the σ -complex of nucleophilic aromatic substitution, it is vital to know what the actual thermal reaction intermediate is if the results are to be used meaningfully in illustrating the photochemical mechanism.

Nature of Chloroaromatic Radicals in Solution.

Scheme III showed the possible sources from which the tetrachlorobenzene radical can abstract a hydrogen atom. It is not clear which of these paths best describe the actual mechanism.

One way to examine the actual nature of the phenyl radical would be to generate a radical free of complexation in the presence of triethylamine and acetonitrile and examine the selectivity of hydrogen atom abstraction. If a similar

relative reactivity occurred in the photochemical reaction, then an unencumbered free radical would be suggested. Russell and Bridger²⁶ did extensive competitive atom abstraction studies using phenyl radicals generated by the thermal decomposition of phenylazotriphenylmethane (PAT). In this work, the 2,3,5,6-tetrachlorophenyl analog was synthesized and allowed to react in the presence of solvent pairs (Scheme VIII).



Scheme VIII

Photochemical Dechlorination in Aqueous Micelles.

Pentachlorobenzene can be dechlorinated, and thus detoxified, by exposure to ultraviolet light. However, typical conditions required for this process do not

lend themselves readily to industrial-scale application. For example, the presence of O_2 in solution rapidly quenches the photoexcited state, thus stopping the reaction, and therefore requiring solution degassing. Also, the organic solvents which must be used to dissolve the compound may be expensive and pose waste disposal problems of their own.

An alternative method for successful photodechlorination is to use aqueous solutions of a surfactant which produces micelles, or self-organized aggregates with a hydrophobic interior volume and a hydrophilic outer surface. The micelles allow solvation of pentachlorobenzene in ordinary water, and by using the appropriate concentrations, dissolved molecular oxygen can be prevented from interacting with the substrate.

Another advantage of studying photochemistry in micelles is the ability to isolate a few or even a single molecule(s) from the bulk phase and therefore to control reaction conditions on a microscopic level. This would allow one to learn about the molecular details of the reaction mechanism. Such applications of micelles to photochemistry have been reviewed.²⁷

Before examining chemical reactions in micelles it is first necessary to discuss their structure. A useful reference here is a review by Ramnath et al.²⁸ There are several proposed models for micelle structure, and although some disagreement exists, the most widely used model is the classical Hartley model (Figure 2). In this model, the micelle is a roughly spherical aggregate with the

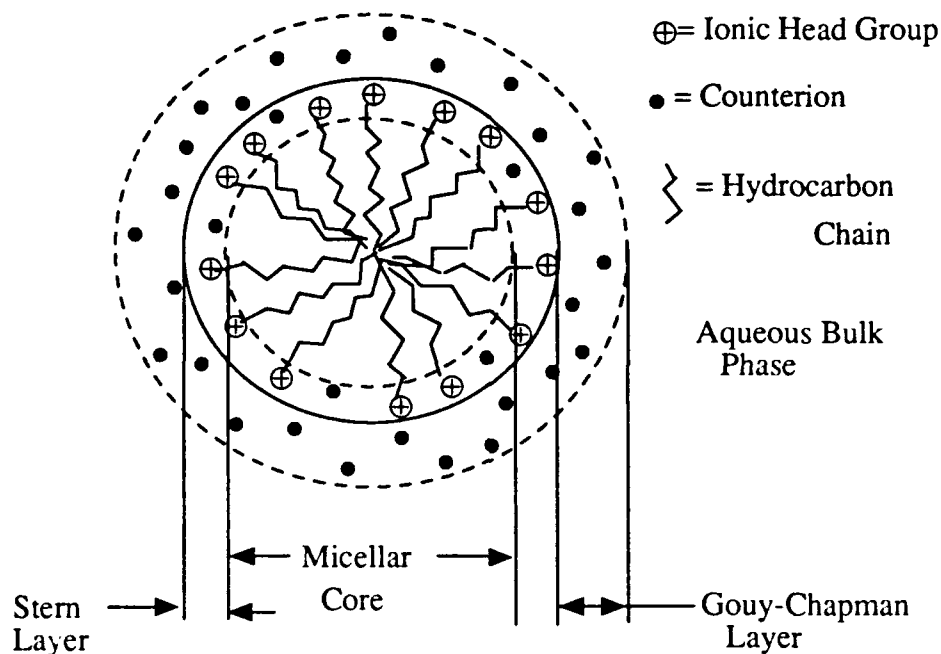


Figure 2. Hartley Model of Micellar Structure.

polar ends of the surfactant defining the surface and the long, nonpolar hydrocarbon chains inside. The Stern layer is a compact region which contains the detergent head groups and counterions, and the Gouy-Chapman layer contains most of the unbound counterions.

Micelles will form in solution if the bulk concentration of the surfactant is above the *critical micelle concentration* (CMC). Below this concentration, micellar structures are absent or in very low concentration. Above this concentration, all detergent molecules are incorporated into micelles. In this study, the surfactant used was cetyltrimethylammonium bromide , $\text{CH}_3(\text{CH}_2)_{15}\text{N}^+(\text{CH}_3)_3\text{Br}^-$. The CMC values for CTAB have been reported (Table 1).²⁹

Table 1. Critical Micelle Concentrations of CTAB
at Various Temperatures.

Temperature (°C)	CMC (M)
25	$5.0 - 9.8 \times 10^{-4}$
35	$9.5 - 10.2 \times 10^{-4}$
45	1.155×10^{-3}

The exact shape of the micelle can vary with concentration and temperature. For CTAB, spherical and rodlike structures define some limiting cases. The structure change can affect photochemical reactivity. For example, in irradiation studies of pyrene, an increase in excimer yield is observed when conditions favoring rodlike micelle structures exist.^{30a} The shapes of CTAB micelles under various conditions have been reported (Table 2).^{30b} In this study,

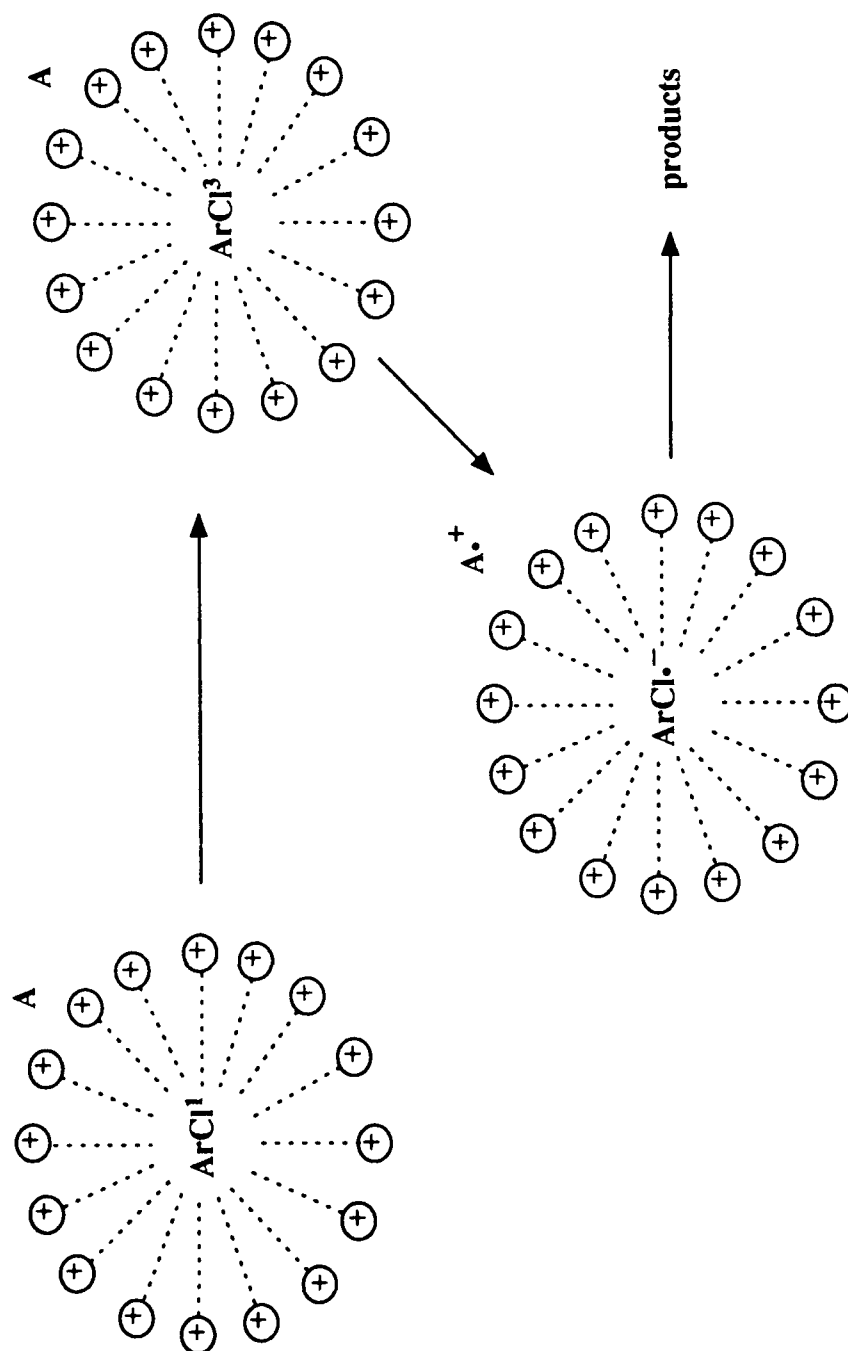
Table 2. Shape Regions of CTAB Micelles at Various
Temperatures and Concentrations.^a

Temp. (°C)	Spherical Micelles	Sphere-Rod Transition	Rodlike Micelles	Middle Phases
70	0.05	0.25		0.32
50	0.05	0.17		0.26
27		0.05	0.10	0.25

^a concentrations in w/w.

reactions were conducted in 0.07 w/w CTAB at about 50 °C, at which the predominant shape should be spherical.

Since an electron donor like triethylamine should exist primarily in the aqueous layer outside the micelle, it is physically separated from the arene by the micelle wall. Therefore, any electron transfer would have to occur across this wall to form the arene radical cation (Scheme IX).

Scheme IX

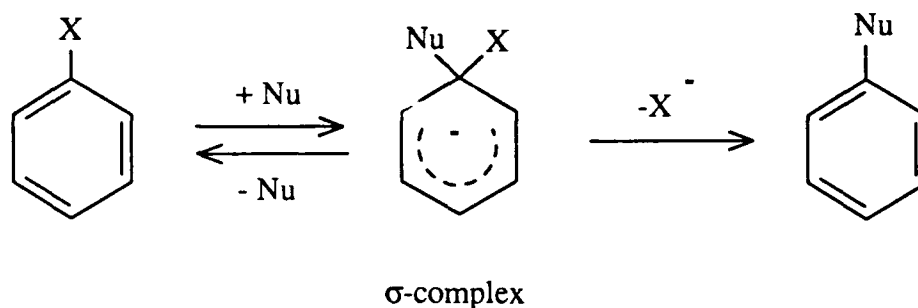
RESULTS AND DISCUSSION

Methoxydechlorination of Pentachlorobenzene.

As discussed in the introduction, the photodechlorination of pentachlorobenzene may proceed via an intermediate radical anion which resembles the σ -complex shown to occur in many types of nucleophilic aromatic substitutions. Since the pentachlorobenzene radical anion dechlorinates to give a regioselective mixture of tetrachlorobenzene isomers, it might be expected that an aromatic nucleophilic addition and subsequent chloride elimination should give a similar regioisomer distribution. Since the reaction with methoxide ion has been shown to proceed smoothly under simple conditions,^{16,17} this reaction was chosen for study and comparison with photochemical results. Before presenting the results, however, it would be helpful to review some theory first.

Nucleophilic aromatic substitution by the addition-elimination (or S_NAr) mechanism is quite different from aliphatic S_N2 nucleophilic substitution.^{19,31,32} In the latter case, the nucleophile approaches the back lobe of the sp^3 orbital which overlaps to form the bond to the leaving group. Such an attack on the back side of the ring carbon sp^2 orbital is not possible in an aromatic system, because this back lobe is shielded from attack by the planar ring system. Instead, the nucleophile uses a vacant π^* orbital and eventually forms a new bond to the attacked carbon atom generating an sp^3 center with the covalent bond to the leaving group still

intact. In this state, the intermediate is called the σ -complex. From this state, either the nucleophile can leave (resulting in the original compound) or the substituent atom can leave (resulting in the substituted compound) (Scheme X).



Scheme X

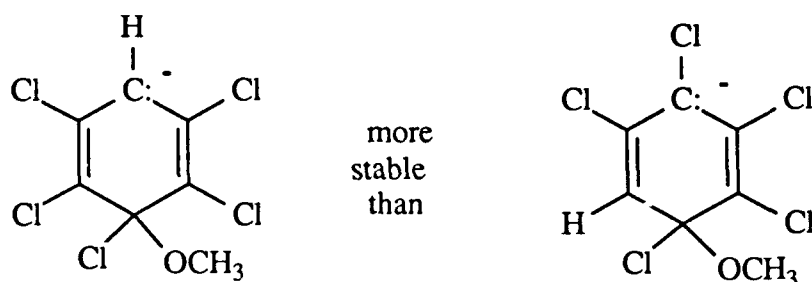
Since the formation of the σ -complex involves loss of aromaticity, it is quite endothermic and does not easily occur unless one or more electron withdrawing substituents are present on the ring in *ortho* or *para* positions. Nitro groups are excellent in this regard. In the case of pentachlorobenzene the presence of five chlorine atoms serves to activate the ring sufficiently to allow nucleophilic attack.

Another interesting contrast to the S_N2 mechanism is the reactivity with regard to halogen leaving (or nucleofugal) groups. In aromatic substitution with methoxide nucleophile, the order of reactivity is $F \gg Cl > Br > I$,^{33,34} which is a reversal of the case in aliphatic substitution. In the latter case, the carbon-halogen bond strength is the rate determining factor and since iodine has the weakest bond,

it proceeds at the fastest rate. In the S_NAr mechanism, however, the rate determining step is the addition of the nucleophile. There are at least two reasons proposed for this trend in aromatic systems. First, since the C-Hal bond dipole is stronger the more electronegative the halogen, the addition of a negatively charged nucleophile is more favored.³¹ Second, since the halogen radii decrease with decreasing atomic number, there would be less repulsion between the nucleophile and, say, fluorine than the other halogens, hence the nucleophile could more easily approach close enough to make a bond.³³

A single electron withdrawing substituent such as a nitro group activates an aromatic ring to nucleophilic attack when it is located *ortho* or *para* to the nucleofugal group. In pentachlorobenzene the directing effects are a bit more complex since there are five electron withdrawing groups and since one of these groups acts as a nucleofuge. Studies have attempted to rationalize the regiochemistry of nucleophilic substitution in aromatic polyhalo compounds.^{14,35} Burdon³⁵ used the so-called I_π repulsion effect to explain regiochemistry in several C_6F_5X compounds. Briefly, this effect is due to electron repulsion between the halogen p -orbitals and the carbon π orbital electrons. The more electronegative the halogen, the more repulsion will result and hence, the less stable will be the negative charge on the carbon atom attached to that halogen. Furthermore, since the *para*-quinonoid structure seems to be favored over the *ortho*-quinonoid structure, the negative charge *para* to the site of nucleophilic attack will predominate. In the pentachlorobenzene case, this implies that the *para* (i.e., 2,3,5,6-tetrachloroanisole, with the methoxy group *para* to the single hydrogen atom) isomer will be favored, since the negative charge will be on a carbon bearing

hydrogen, which is less destabilizing than one bearing chlorine:



Chambers et al.¹⁴ have reported detailed quantitative studies of the effects of chlorine and fluorine atoms in various ring positions on nucleophilic attack in both benzene and pyridine compounds. The inductive effects of chlorine atoms tend to stabilize a nearby negative charge, and the I_π repulsion tends to destabilize an adjacent negative charge. Chlorine is found to be least stabilizing in a *para* position, and increasingly stabilizing in *meta* and *ortho* positions, relative to the position of nucleophilic attack. The values from this work for the activating influence of chlorine atoms to nucleophilic aromatic attack by methoxide ion are (relative to hydrogen at the same position) *ortho* = 182.4, *meta* = 73.14 and *para* = 15.05.

By applying these factors to pentachlorobenzene, the relative rates at the various positions for an S_NAr -type substitution are predicted to be as shown in Figure 3.

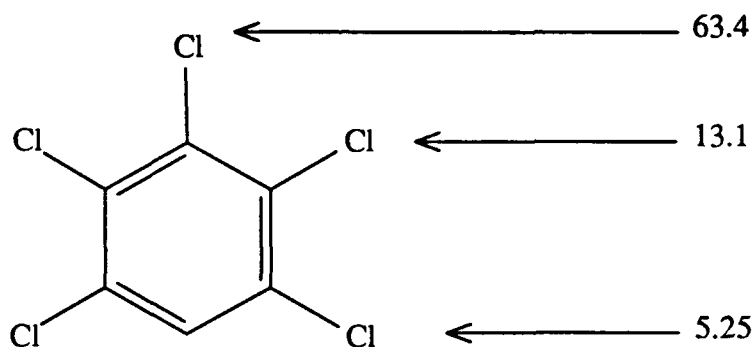


Figure 3. Calculated Relative Reactivities of Pentachlorobenzene Chlorine Atoms.

The first experimental test of this reaction was done in pyridine/methanol following a procedure similar to that of Yakobson et al.¹⁶ Several conditions were tested, each varying the pyridine:methanol ratio. In each case, pentachlorobenzene concentration was 0.1 M, and the reactions were conducted at 93 °C. Assuming in advance that the reaction kinetics would be second order, the kinetics were measured by following the disappearance of the starting material. Integration of the general expression for second order kinetics gives the solution:

$$kt = \frac{1}{(B_0 - A_0)} \ln \frac{A_0 B}{B_0 A}$$

If $B_0 = A_0$, this simplifies to:

$$kt = \frac{1}{A_{(t)}} - \frac{1}{A_0}$$

In this experiment, the initial concentration of pentachlorobenzene ([PCB]) was set equal to methoxide ion concentration ([MeO⁻]), so that use of this latter kinetic expression is valid. This expression was further modified so that measurable quantities such as initial concentrations and gas chromatographic peak integration areas could be used (see appendix A). Gas chromatographic integrated peak areas were measured relative to an internal standard, *para*-dimethoxybenzene, which was shown to be inert to the reaction conditions.

In pyridine/methanol mixtures, this analysis yielded a linear correlation (with R² values better than 0.95), which is consistent with second-order kinetics. In a 3:1 v/v mixture of pyridine:methanol, the rate constant was measured as $9.05 \times 10^{-4} \text{ M}^{-1}\text{sec}^{-1}$. In an 8.2:1 mixture, the rate constant was $5.51 \times 10^{-2} \text{ M}^{-1}\text{sec}^{-1}$.

Although the *para*- and *meta*-tetrachloroanisole products were not resolved by GC, the relative percentage of this combined isomer peak and the *ortho*- isomer were calculated. At low conversions, the percentage of *ortho*- isomer was 22-23%, and at higher conversions, the percentage was 24-26%. This is significantly lower than that reported by Yakobson et al.,¹⁶ who reported 33-38% *ortho*- isomer. At this point, this disparity was not resolved.

A side reaction in this solvent system was made evident by the drastic color change of the reaction mixture. Initially colorless, the solution became yellow, then orange, red and finally dark brown. Upon addition of acetic acid, these

solutions turned deep violet. The color of the acidified solution gradually faded to amber over the next few days. These color changes did not take place in heated solutions containing only pyridine and methoxide ion. It is known that certain pyridinyl radical compounds are strongly colored and can exist at room temperature for several days.³⁹ Although difficult to conceive of, perhaps some electron transfer reaction was responsible for this color generation. At any rate, some combination of the reactants apparently was producing unidentified products. Therefore, due to the uncertainties presented by this apparent side reaction, the pyridine:methanol system was abandoned.

A much cleaner reaction occurs at lower temperatures in DMSO:methanol mixtures,¹⁷ so further kinetics were studied in this system. In general, pentachlorobenzene and methoxide ion concentrations were set equal at 0.01 M and *para*-dimethoxybenzene was again used as an internal standard. Reactions were run at 50.0 ± 0.1 °C. Several different ratios of DMSO:methanol were tested, and the reaction rate increased for higher fractions of DMSO. In 13.9:1 mixtures, the second-order kinetic plots again yielded straight lines with linear regression analysis giving R^2 values of at least 0.99. An average rate constant was calculated to be $2.26 \times 10^{-1} \text{ M}^{-1}\text{sec}^{-1}$ with a standard deviation of 3.65×10^{-3} .

Before discussing product ratios in this reaction, some observations about solvent effects on rate will be discussed. It is known that polar aprotic solvents accelerate the rate of nucleophilic aromatic substitution reactions.^{31,32} This is attributed to the poor solvation of the negatively charged nucleophile, an effect which enables it to more easily approach and react with an electrophilic substrate. On the other hand, hydroxylic solvents tend to highly solvate the anion, thus

encumbering it and interfering with nucleophilic attack. Thus, it would appear that if this trend were followed for the methoxydechlorination reaction, a small piece of evidence in favor of the S_NAr mechanism would have been obtained.

As mentioned, reactions in several mixtures of DMSO:methanol were studied. Additionally, polar hydroxylic and nonpolar solvent systems were studied. Table 3 summarizes the results of these studies, and includes solvent dielectric constants⁴⁰ for comparison. A linear regression analysis of the

Table 3. Rate Constants for Pentachlorobenzene
Methoxydechlorination in Various Solvent Systems.

Solvent	Solvent:CH ₃ OH Ratio	Dielectric Constant	<i>k</i> (M ⁻¹ sec ⁻¹)
DMSO	61 : 1	47	5.708
	38 : 1		3.155
	13.9 : 1		0.23
	9 : 1		0.14 ^a
Pyridine	8.2 : 1	12	0.055
	3 : 1		0.00091
Toluene	8.3 : 1	2.3	^b
Methanol	---	32.7	^b

^a From Reference 17. ^b No reaction at 100°C, 3 hr.

DMSO:methanol mixture results shows a linear dependence of the rate constant on the mixture ratio with a slope of 0.111 M⁻¹sec⁻¹ and a correlation coefficient R^2 of

0.995. A look at Table 3 confirms that a rate enhancement in accordance with an S_NAr mechanism is occurring.

In order to test for the possible existence of radical intermediates in this reaction, the kinetics were studied in the presence of a radical trap, galvinoxyl (Figure 4). This compound has been used successfully as a trap in $S_{RN}1$ reactions,

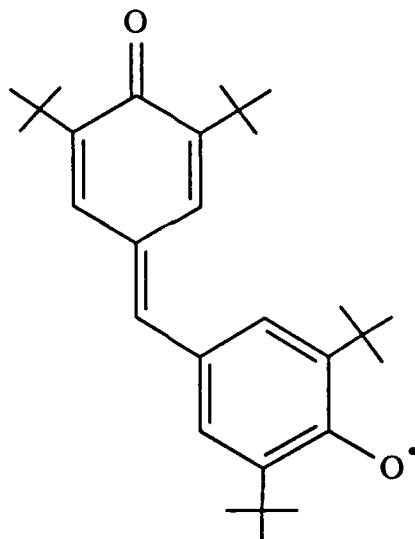


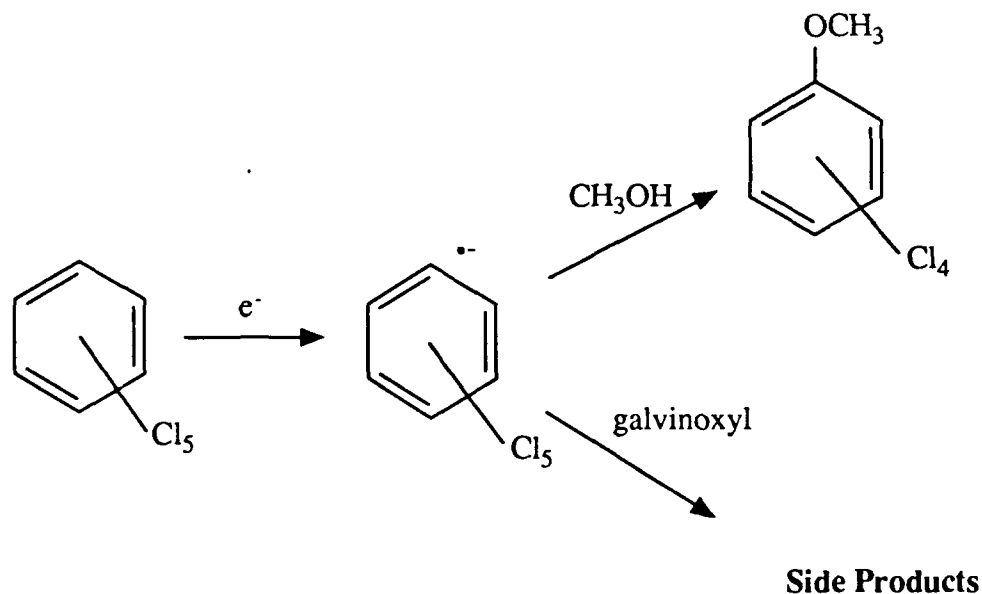
Figure 4. Galvinoxyl

and reaction rate retardation was observed using 5-10 mol% galvinoxyl.⁴¹ Galvinoxyl is stable to oxygen in the solid state, and reacts only slowly with oxygen in solution, so no strict degassing of solvents is necessary. It is known to combine quantitatively with a number of radicals.⁴²

The reaction in 13.9:1 DMSO:methanol done in this work was repeated in

the presence of 5 mol% (relative to pentachlorobenzene) galvinoxyl. Again, a second order plot was linear, with R^2 of .994, and yielding a rate constant of $2.16 \times 10^{-1} \text{ M}^{-1}\text{sec}^{-1}$ ($\pm 5.13 \times 10^{-3} \text{ M}^{-1}\text{sec}^{-1}$). This rate is very slightly lower than that found for reactions without galvinoxyl, but this difference is not considered significant. A second-order kinetic plot is included in Appendix B.

It must also be considered that the effect of galvinoxyl may not be seen on the rate of disappearance of pentachlorobenzene but on the rate of formation of products. For example, Scheme XI shows a situation where this could be true.



Scheme XI

To check for this, the reaction rate as a function of product formation, the mass balance of the reaction was checked from the gas chromatograms. It was

found that the combined mass of pentachlorobenzene and known products was constant to within $\pm 2\%$ of the starting pentachlorobenzene concentration (relative to internal standard) with no discernable trend from sample to sample. This demonstrates that galvinoxyl does not interfere with the rate of product formation. It was also found that the relative amounts of product isomers were not changed. It appears, therefore, that galvinoxyl does not affect the rate of reaction, nor does it alter product formation in any way.

Since two of the three product isomers could not be resolved by gas chromatography, another method of analysis was required. As part of a search for an alternate method, it was determined that ^1H nuclear magnetic resonance spectroscopy could resolve and quantitatively measure the isomers by examining the aromatic ring proton signal. The ring proton on each of the three isomers and pentachlorobenzene were easily resolved, and a NMR spectrum of a standard mixture of these 4 compounds is shown in Appendix B. To remove the interference of other signals in the NMR, the GC peak containing the *para*- and *meta*-tetrachloroanisole isomers was isolated by preparatory GC. From this, the relative amounts of these two isomers could be established; then using previous GC data, the amounts of each relative to the *ortho* isomer could be calculated. Table 4 shows the results of this analysis from three of the DMSO:methanol experiments (Number 3 is from one of the galvinoxyl experiments).

Table 4. Tetrachloroanisole Product Isomer Relative Percentages.

Sample	Relative Percentages		
	<i>para</i>	<i>meta</i>	<i>ortho</i>
1	50.8	22.6	26.6
2	49.4	23.8	26.8
3	48.0	25.5	26.5
Average	49.4 \pm 1.4	24.0 \pm 1.5	26.6 \pm 0.15

These results, as well as the results from the pyridine:methanol mixture reactions, are notably different from the previously reported values of about 54:10:36 for *para:meta:ortho*.¹⁶ A possible explanation for this discrepancy was discovered rather serendipitously while performing some further test reactions in the DMSO:methanol system. Upon analyzing several mixtures which had been conducted at various temperatures, it was noted that samples run at room temperature showed relative percentages of *ortho*-tetrachloroanisole of as low as 22%, while those run at above 75 °C had as high as 48%! In addition, the GC spectra of mixtures with high amounts of *ortho* isomer also showed a number of small new peaks.

In an attempt to shed light on this puzzle, a sample containing higher amounts of the *ortho* isomer were submitted for GC-mass spectroscopic analysis. The results were quite revealing. The new small peaks and a major portion of the "*ortho*" peak had nearly identical mass spectra, with molecular ion of $m/e = 246$, and showed a pattern characteristic of 3-chlorine compounds. Copies of representative spectra are included in Appendix B. Based on these spectra, it was postulated that these unknown products were the result of further methoxydechlorination of the primary tetrachloroanisole products. Six peaks showed the same pattern, and this is consistent with the 6 possible regioisomers of trichloro-dimethoxybenzene (Figure 5).

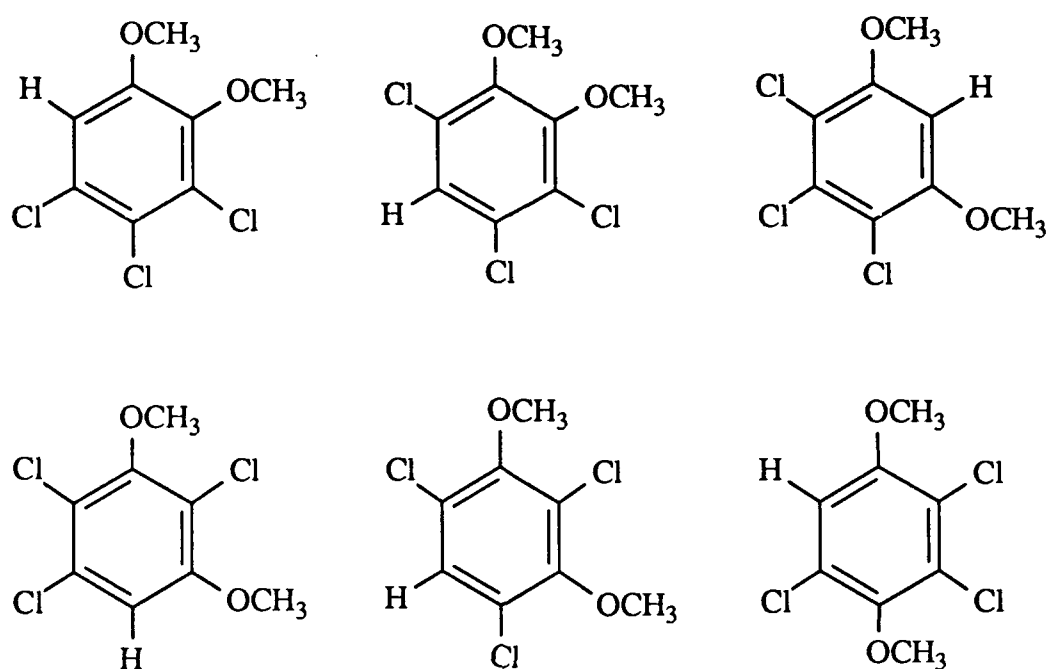


Figure 5. Trichlorodimethoxybenzene Isomers.

Upon rechecking the calculation of reactant concentrations for these reactions, it was discovered that an error led to the addition of a twofold excess of methoxide ion. This excess allowed the reaction to continue beyond monosubstitution to produce significant amounts of the disubstituted products, even before the complete conversion of pentachlorobenzene. Interestingly, previously cited reactions of pentachlorobenzene in pyridine and DMSO^{16,17} used excess methoxide ion (twofold and 70% excess, respectively) and also analyzed samples by gas chromatography. It may be that the *ortho* percentages (35% and 29%, respectively) reported by these workers were raised by the same disubstitution observed here.

Now being aware of a possible interference in the analysis of primary products, the next question was to check whether the data from the previous runs was in error. An experiment to test the relative rates at which the three tetrachloroanisole isomers react with a second equivalent of methoxide was conducted. Upon separately reacting the three isomers with methoxide, it was shown that the *para* isomer produced two products in relative yields of 10:1, with about 13% conversion of the starting material. The major of these two products showed a GC retention time equal to that of the *ortho* isomer. The *meta* isomer gave products which had retention times between the *para* and *ortho* peaks (exact assignment was difficult due to an impurity in the starting material which showed additional impurities upon reaction). The *ortho* isomer showed one minor product on the GC trace, and also showed a small amount of another product by GC-MS analysis with a retention time coincident with the starting material, with a conversion of about 3%. From this it was concluded that *para*-tetrachloroanisole is the major contributor to the excess found in the "*ortho*" GC peak.

GC-MS analysis of a previous reaction mixture from the kinetic experiments in DMSO showed about 10% of the disubstituted product in the *ortho* peak. Estimating that 8% of this impurity originated from *para*-anisole, then a corrected isomer distribution was calculated and is presented in Table 5.

Table 5. Tetrachloroanisole Product Composition.

Sample	Relative Percentages		
	<i>para</i>	<i>meta</i>	<i>ortho</i>
1 ^a	50.8	22.6	26.6
2 ^a	49.4	23.8	26.8
3 ^b	48.0	25.5	26.5
Average :			
Uncorrected	49.4 ± 1.4	24.0 ± 1.5	26.6 ± 0.15
Corrected ^c	51.5 ± 1.5	24.0 ± 1.5	24.5 ± 0.14

^a Reaction run without galvinoxyl. ^bwith galvinoxyl.

^c Corrected for further dechlorination using GCMS data.

These experiments and other factors suggest that the mechanism of methoxydechlorination of pentachlorobenzene is consistent with the S_NAr mechanism. The S_{RN}1 mechanism is unlikely for the following reasons:

1. The kinetics exhibit a second-order behavior to high precision. A radical chain mechanism would be expected to show more complex behavior.
2. No effect on reaction rate or product ratio was seen in the presence of a radical trap which has been shown to inhibit S_{RN}1 reactions.
3. Formation of tetrachlorobenzene would be expected if a

tetrachlorophenyl radical intermediate were involved, as would be true in an $S_{RN}1$ scheme. No tetrachlorobenzene products were detected.

4. A solvent effect similar to that seen in S_NAr reactions^{31,32} was observed for this system.

5. This system is not expected to show $S_{RN}1$ behavior *a priori* because of the nucleophile used. It has been reported^{21,22} that alkoxide nucleophiles are unreactive in $S_{RN}1$ reactions, so the above results are not surprising.

It is still conceivable that the reaction involves electron transfer with associated radical pairs, for example, as proposed by Bunton (see Scheme VII, Introduction Section). This could be checked by performing the same NMR and UV experiments which were done by that group. Electron spin resonance spectroscopy might show a radical intermediate, however others have reported that no such intermediates were seen in systems without nitro activating groups.²² However, for the purposes of this study, such an electron transfer intermediate pathway is not important, since the reaction proceeds through the σ -complex before going on to product, so the same regiochemistry would be expected.

Now that it is reasonably certain that this mechanism is S_NAr , it remains to compare the results to those obtained from photochemical experiments and to those predicted from theory. Table 6 presents the regiochemical results for various conditions.

Table 6. Comparison of Regiochemistry of Products from
Photo- and Methoxydechlorination of Pentachlorobenzene.

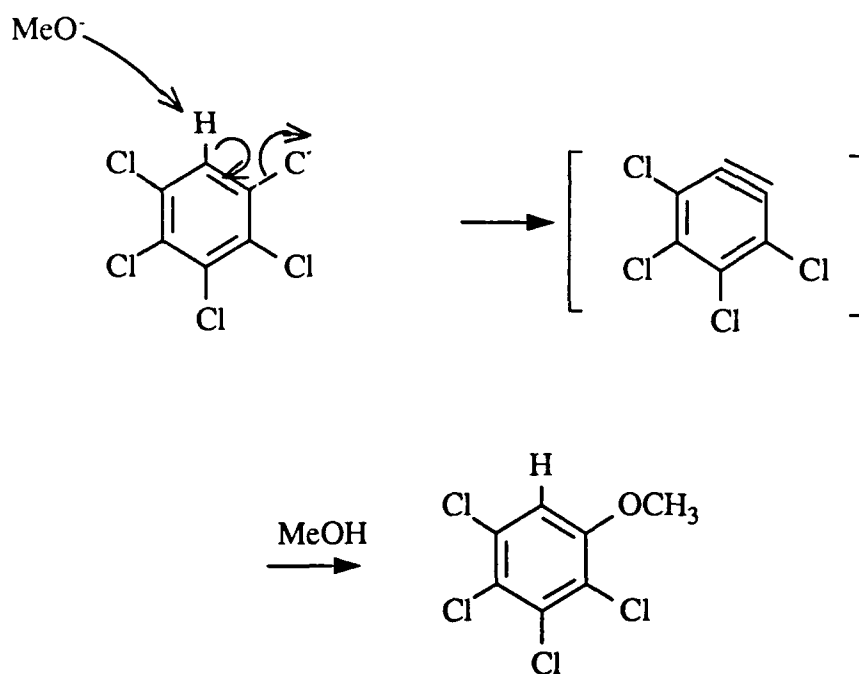
Conditions	Relative Percentages		
	<i>para</i>	<i>meta</i>	<i>ortho</i>
DMSO:MeOH, MeO ⁻ , 50 °C	51.5	24.0	24.5
Predicted ^a	63.4	26.2	10.5
hν, CH ₃ CN, ^b Et ₃ N	66.21	25.32	8.47
hν, CH ₃ CN ^c 0.011 M ArCl	38.53	45.95	17.6

^apredicted using data of reference 14. ^bRef. 10. ^cRef. 9.

It is apparent that thermal nucleophilic substitution gives regiochemistry which is closer to the photochemical reaction run in the presence of triethylamine than to that run without triethylamine.. However, the amount of *ortho* isomer is substantially higher than for the photochemical case. The probable reason for this is steric. In nucleophilic substitution, a nucleophile must approach a carbon atom connected to a large chlorine atom. Certainly, the chlorine atom *ortho* to the aromatic ring hydrogen atom is the most easily approachable since it only has one adjacent chlorine atom. In fact, it has been reported that for very bulky

nucleophiles such as diethylamine, substitution of pentachlorobenzene occurs almost exclusively (82%) at the *ortho* position. It is reasonable to assume, then, that the less bulky methoxide nucleophile might have a much smaller but still significant steric effect.

There is another possible reason for the high *ortho* percentage. It is well known that in the presence of a strong base, haloarenes can dehydrohalogenate to yield a benzyne intermediate (Scheme XII). In the presence of a nucleophile, the



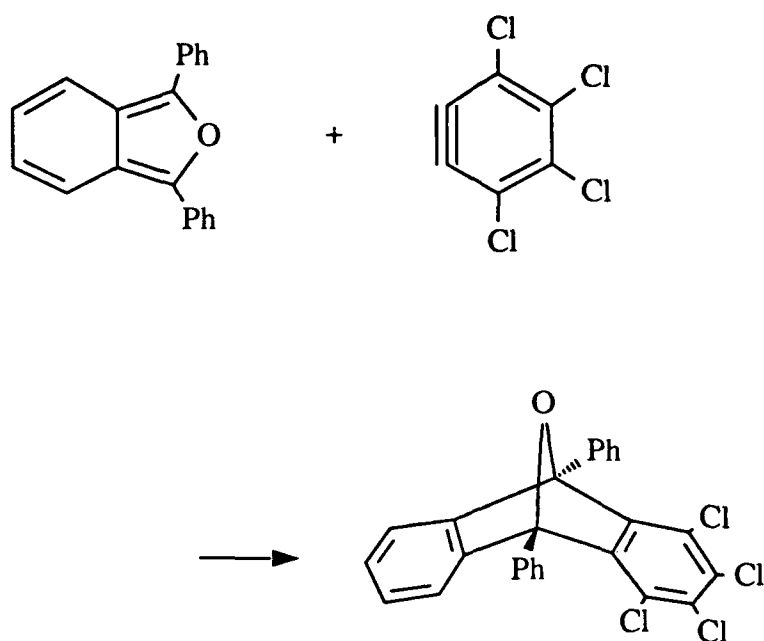
Scheme XII

benzyne can capture the nucleophile, thus producing an *ortho* substituted

compound. In the case of pentachlorobenzene in methanol, the product would be *ortho*-tetrachloroanisole, and a source of "excess" *ortho* isomer would be possible.

Methoxide ion is not normally considered to be basic enough to induce dehydrohalogenation. However, the basicity is substantially increased in DMSO, where pK values go from 15.5 in water to 29.0 in DMSO.⁴³ Additionally, the acidity of the ring proton in pentachlorobenzene is relatively high for an aromatic system.⁴⁴

In order to test for a possible benzyne mechanism, a compound which efficiently traps the intermediate was used. Such a compound is 1,3-diphenylisobenzofuran,^{45,46} which acts as a diene in a $[4 + 2]$ cycloaddition, with benzyne as the dienophile (Scheme XIII).

**Scheme XIII**

In this experiment, the isobenzofuran was added in 14 mol% relative to pentachlorobenzene. The reaction was run through approximately 2 half-lives of pentachlorobenzene. The relative amount of *ortho* isomer in the trapped reaction was 26.0%, while in a simultaneously run untrapped reaction it was 26.1%. It is apparent that no reduction in formation of this isomer had occurred, and a benzyne mechanism can be ruled out.

In conclusion, it appears that the thermal nucleophilic substitution reaction of pentachlorobenzene with methoxide ion follows the standard S_NAr mechanism.

This fact makes the reaction a useful model in studying the regiochemistry of photodechlorination of pentachlorobenzene in the presence of triethylamine. The regiochemistry of the methoxydechlorination is roughly in accord with the photochemical regiochemistry, however, the amount of *ortho* isomer is higher than expected. This is most likely due to the reduced steric hindrance involved with nucleophilic attack at the *ortho* site. Taking this into account, these results support the hypothesis that the pentachlorobenzene radical anion produced photochemically in the presence of Et₃N fragments to generate the tetrachlorophenyl radical via a bent transition state analogous to the S_NAr substitution σ -complex intermediate.

Reactions of Thermally Generated Tetrachlorophenyl Radicals.

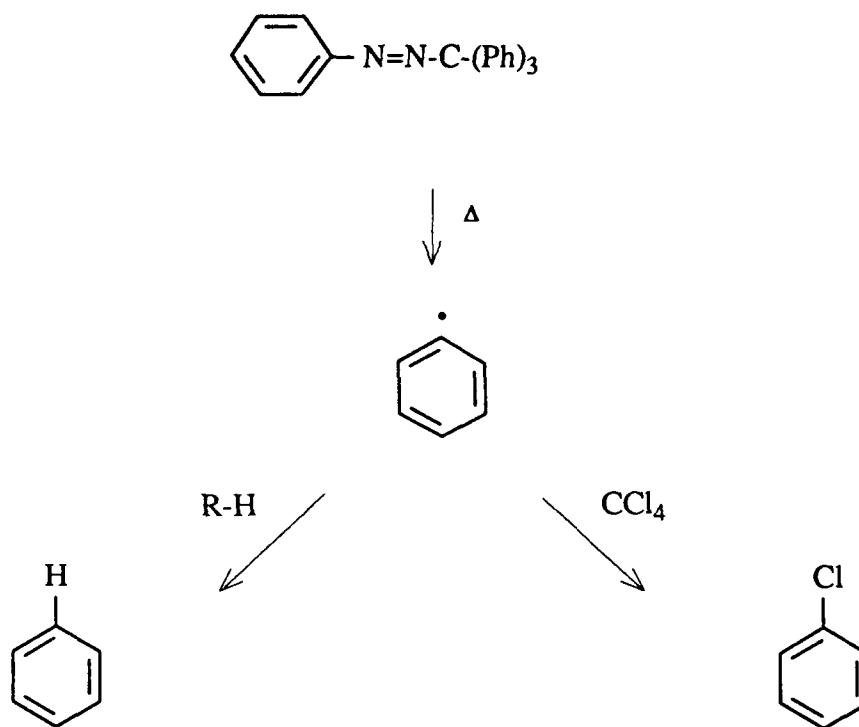
Studies have presented evidence for the involvement of a radical anion excimer complex intermediate during photolysis of pentachlorobenzene in acetonitrile in the presence of triethylamine^{9,12} (Scheme III, Introduction Section). However, it is not clear whether the ultimately formed tetrachlorophenyl radical abstracts a hydrogen atom from the triethylamine radical cation associated in the cage, or whether it escapes into the bulk solvent and can abstract a hydrogen atom from either acetonitrile or other triethylamine molecules.

In an attempt to answer this question, Ramnath³⁶ studied this photochemical reaction using trideuterioacetonitrile (CD₃CN) as a solvent. If the radical were able to escape into the bulk solvent, it should competitively abstract

deuterium from this solvent as well as hydrogen from the added triethylamine. In fact, the results of this experiment were ambiguous. In solutions of 0.05 M pentachlorobenzene and 2.0 M triethylamine in CD_3CN , only 1.7% of the tetrachlorobenzene products had incorporated deuterium. When triethylamine was replaced by diazabicyclo[2.2.2]octane (DABCO), which should be a very much poorer hydrogen atom donor than triethylamine (and should therefore significantly boost deuterium incorporation), only a modest increase to 6.4 % was seen. Since *some* deuterium incorporation was occurring, it seemed that the radical had access to the bulk solvent. However, the fact that only a small amount of deuterium was incorporated in an environment overwhelmingly rich in deuterium atom donor was puzzling.

It was considered that another method could be used to check this hypothesis. A thermally generated free tetrachlorophenyl radical in the presence of two different atom donors would show the selectivity of the unencumbered radical towards atom abstraction. The results of such a competitive study could then be compared to the results of the photochemical experiment, and thus provide support for one of the two proposed pathways.

An extensive study of this type was done with phenyl radical by Bridger and Russell in 1963.²⁶ In their study, phenyl radical was generated by the thermal decomposition of phenylazotriphenylmethane (PAT). In the presence of carbon tetrachloride and a hydrogen atom donor R-H, either benzene or chlorobenzene would be formed (Scheme XIV), with the ratio of the two related to the ratio of the

**Scheme XIV**

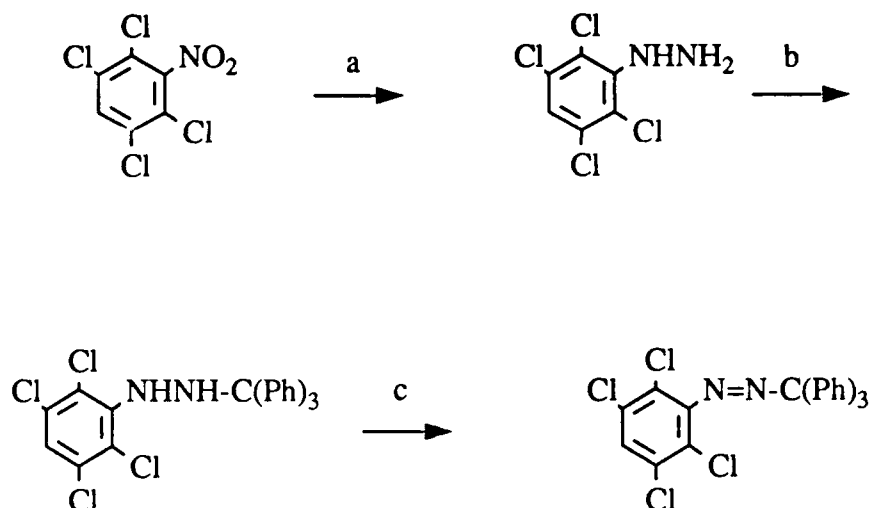
rate constants for atom abstraction by the expression:

$$\frac{k_{\text{H}}}{k_{\text{Cl}}} = \frac{[\text{C}_6\text{H}_6] [\text{CCl}_4]}{[\text{C}_6\text{H}_5\text{Cl}] [\text{RH}]}$$

This equation relies on three assumptions: (1) the atom abstraction reactions are first order in RH and CCl_4 and are of the same kinetic order in $\text{C}_6\text{H}_5^\bullet$; (2) the reactions shown in Scheme XIV are the only sources of benzene and

chlorobenzene; and (3) the ratio $[\text{CCl}_4]/[\text{RH}]$ remains constant. The first assumption was shown to be valid by several kinetics studies, and based on the similarities of the phenyl compound with the tetrachlorophenyl compound, it is assumed that this would also be true for the latter compound. The second assumption is not completely true, but it can be approximately corrected for. Upon reacting the azo compound in pure CCl_4 , formation of a small amount of benzene was observed, presumably from reaction of the phenyl radical in a cage with PAT or other decomposition products. By measuring the amount of hydrogen atom abstraction, a correction can be made to the $[\text{C}_6\text{H}_6]$ term in the relative rate equation. Finally, the third assumption turns out to be valid because of the choice of triphenylmethyl radical as the other radical formed in decomposition. Since this is known to be a relatively stable radical, it builds up to an appreciable steady-state concentration and thereby prevents the occurrence of radical-chain processes. Therefore, the only significant consumption of RH and CCl_4 is in a one-to-one ratio by phenyl radical, which reduces solvent concentrations by less than about 1%.

For this study, 2,3,4,5-tetrachlorobenzeneazotriphenylmethane (TCBAT) was prepared by using the synthesis outlined in Scheme XV.³⁷

**Scheme XV^a**

^a(a) NH₂NH₂ hydrate, 95% EtOH; (b) (Ph)₃CCl, THF;
 (c) 2,4,6-triphenylphenol, K₃Fe(CN)₆/2N aq. NaOH, CH₂Cl₂.

After careful recrystallization, the compound was analyzed by NMR and UV spectroscopy (See Appendix C) and stored in a freezer until used for reactions.

The reactivity of this tetrachlorophenyl compound might be expected to show some differences from the PAT compound due to the effect of four ring chlorine atoms. For example, the PAT compound was observed to have a decomposition rate constant of about $8.0 \times 10^{-4} \text{ sec}^{-1}$ at 64 °C, and about $2 \times 10^{-4} \text{ sec}^{-1}$ at 53.35 °C.³⁷ These rate constants correspond to half-lives of about 15

minutes and 60 minutes, respectively. Interpolation to 60 °C using the Arrhenius equation gives a half-life of about 20 minutes. Based on evidence presented by Cohen and Wang³⁷ chlorine substitution should slow the rate of decomposition. In that work, they demonstrated that both electron-attracting *and* electron-repelling groups in a *para* position slow the rate of decomposition. For example, the rate of decomposition of *para*-bromo PAT was 2.14 times slower at 53.35 °C than for unsubstituted PAT.

A study of the decomposition kinetics of TCBAT was done at 60 °C using UV/VIS spectroscopy to measure the disappearance of the starting material. This compound shows a characteristic absorbance at $\lambda_{\text{max}} = 420 \text{ nm}$ ($\epsilon = 25.2 \text{ M}^{-1}\text{cm}^{-1}$). At 60 °C, it was found that the half-life of TCBAT in CCl_4 was 104 minutes, which gives a rate-constant of $1.11 \times 10^{-4} \text{ sec}^{-1}$. The plot is included in Appendix C. This rate of decomposition is slower than that for PAT by a factor of 5. In order to speed this reaction to a practical rate, a higher temperature was tested. At 75 °C, the rate was measured as above and was found to be 16 minutes, which gives a rate constant of $7.22 \times 10^{-4} \text{ sec}^{-1}$. Using these two rate constants, an estimate of the activation energy (E_a) can be found from the Arrhenius equation. From these two experiments, E_a was found to be 28.7 kcal/mol.

Other characteristics of this reaction may change as well. As mentioned earlier, PAT produced 5% benzene even though the reaction was done in CCl_4 , suggesting that either some degree of cage reaction is occurring or that some of the phenyl radical is abstracting hydrogen from another PAT molecule, or both. The structural differences in TCBAT may alter the amount of this path of hydrogen atom abstraction. Also, relative reactivities toward RH versus CCl_4 might be

affected, since abstraction of a chlorine atom to form pentachlorobenzene introduces steric strain between two *ortho* chlorine atoms not present in chlorobenzene.

Analysis of reaction mixtures in pure CCl_4 showed a significant increase over PAT in the amount of hydrogen-abstraction product. Mixtures which showed no remaining TCBA in the UV/VIS spectrum contained 24.5% *para*-tetrachlorobenzene and 75.5% pentachlorobenzene. This correction must, therefore, be applied to subsequent calculations.

It now remained to determine $k_{\text{H}}/k_{\text{Cl}}$ values for various hydrogen atom donors. Reactions were run in sealed, degassed ampoules, each containing 0.500 mL of a 0.1 M TCBA solution. The solvent mixtures were proportioned such that roughly equal amounts of the penta- and tetrachlorobenzenes would result, however, the actual results sometimes heavily favored one product. The correction to tetrachlorobenzene was made by subtracting 32.5% of the pentachlorobenzene peak area from the tetrachlorobenzene GC peak. Results are presented in Table 7.

These results show that 1,2,4,5-tetrachlorophenyl radical overwhelmingly favors hydrogen atom abstraction from triethylamine, DABCO and quinuclidine over deuterium atom abstraction from CD_3CN . While the experimental error is large, it is clear that the rate of hydrogen atom abstraction relative to abstraction of a deuterium atom from CD_3CN ($k_{\text{H}}/k_{\text{D}}$) in these experiments is comparable to that for photochemical experiments run in triethylamine. In DABCO, the photochemical experiment seems to favor hydrogen abstraction by about 4 times more than was found in this experiment. Given the error here and potential error in the photochemical experiments, it may be that these results are all essentially

Table 7. Selectivity of Tetrachlorophenyl Radical at 75 °C.

Substrate	$\frac{[\text{CCl}_4]}{[\text{RH}]}$ ^a	$\frac{[\text{C}_6\text{H}_2\text{Cl}_4]}{[\text{C}_6\text{HCl}_5]}$ ^b	$\frac{k_{\text{H}}}{k_{\text{Cl}}}$ ^c	$\frac{k_{\text{H}}}{k_{\text{D}}}$ ^d
CD ₃ CN	0.361	1.61 ± 0.054	0.581 ± 0.020	1
Et ₃ N	108.1	36.5 ± 12.5	3946 ± 1351	6621 ± 2337
DABCO ^e	29.8	49.2 ± 3.8	1466 ± 113	2524 ± 213
Quinuclidine	35.6	38.3 ± 1.1	1364 ± 39	2348 ± 105
hv, CD ₃ CN with: ^f				
Et ₃ N (0.165 M)				6430
DABCO (0.025 M)				11938

^a[RD] when CDCl₃ is used. ^b[C₆HDCl₄] when CD₃CN used. ^cCorrected, average. ^drate of hydrogen atom abstraction from RH relative to rate of deuterium abstraction from CD₃CN. ^ediazabicyclo[2.2.2]octane. ^fReference 36.

equal. This would support the photochemical mechanism in which the pentachlorobenzene radical anion fragments to the tetrachlorophenyl radical and abstracts a hydrogen atom while free in solution.

Photochemistry of Pentachlorobenzene in Micelles.

The purpose of this experiment was to investigate the effects of triethylamine on the rate of photodechlorination of pentachlorobenzene in undegassed aqueous micellar solutions. Before reviewing experimental results, however, it would be useful to discuss solution statistics of CTAB micellar solutions.

In aqueous CTAB solutions, pentachlorobenzene is dissolved within the micelle core. This effectively increases the concentration of pentachlorobenzene relative to what it would be if it were dissolved in the same volume of solution in the absence of CTAB. This higher concentration is referred to as the *microscopic concentration* and can be calculated using the equation:

$$C_m = \frac{C_b}{C_s V_{hc}}$$

where C_b is the bulk concentration of the solute, C_s is the CTAB concentration and V_{hc} is the partial molal volume of the hydrocarbon region of the

micelle.⁴⁷ A useful rule of thumb states that partial molal volume can be estimated assuming that each methyl or methylene group in the CTAB hydrocarbon chain contributes 18 mL/mol.⁴⁸ This makes $V_{hc} = 0.288$ L/mol CTAB. Using this value together with $C_b = 0.001$ M and $C_s = 0.20$ M gives a microscopic concentration $C_m = 0.0174$ M.

The distribution of pentachlorobenzene molecules among the micelles is governed by Poisson statistics.²⁷ The probability of finding a micelle containing n solute molecules is given by:

$$P(n) = \frac{\langle s \rangle^n}{n!} \exp(-\langle s \rangle)$$

where the mean occupancy number $\langle s \rangle$ is the ratio of the bulk concentration of pentachlorobenzene to the bulk concentration of micelles:

$$\langle s \rangle = \frac{[\text{Solute}]}{[\text{Micelles}]}$$

the latter of which is given by:

$$[\text{Micelles}] = \frac{[\text{CTAB}] - \text{CMC}}{N_{agg}}$$

where N_{agg} is the mean aggregation number of CTAB molecules per micelle and is assumed to be 80.⁴⁹ A table of Poisson distribution probabilities at various values of $\langle s \rangle$ is presented in Appendix D.

As discussed earlier, triethylamine changes the product composition of photodechlorination in degassed acetonitrile solution. In the presence of triethylamine, photoexcited pentachlorobenzene forms a radical anion, which undergoes chlorine fragmentation by a different mechanism than does the triplet excited state.

In micellar solutions, it may be possible for the same type of charge transfer to occur between triethylamine and pentachlorobenzene while physically separated by the micelle wall. Such an effect was apparently observed in degassed micellar solutions.¹² Data illustrating each of the above conditions is presented in Table 8.¹² In order to compare these data with further experiments, a microscopic concentration of 0.0174 M pentachlorobenzene was used, which makes the predominant micelle occupancy number ≤ 1 .

The experiments in this study were conducted in 0.200 M aqueous CTAB solutions and were irradiated using an ordinary sun lamp. In one of the runs, triethylamine was added in 0.165 M concentration. Gas chromatographic analysis was made very difficult by the presence of many strong impurity peaks, most of which were identified by GC-MS as C₁₀ through C₁₈ straight and branched alkanes, presumably due to contamination of the CTAB or degradation of the cetyl moiety. The results showed a slightly higher reaction rate in the absence of triethylamine, which is the reverse of what is expected. The regioisomer distribution of the tetrachlorobenzene products from the irradiation in the presence of triethylamine is unlike that from any of the other previous experiments (Table 9). Plots of the relative concentrations of starting material and products versus

Table 8. Relative Ratios of Products from the Irradiation of Pentachlorobenzene.

Medium (Concentration)	Statistical Probability of Micelle Occupancy					% Ratio of Products ^a		
	0	1	2	3	4	<i>meta</i>	<i>para</i>	<i>ortho</i>
CH ₃ CN (0.005 M)						48.4	39.5	12.1
CH ₃ CN (0.071 M)						40.3	40.3	19.4
CTAB ^b (0.017 M) ^c	0.673	0.267	0.053	0.007	0.001	49.8	45.1	5.10
CTAB ^b (0.174 M) ^c	0.018	0.072	0.144	0.194	0.195	43.6	51.0	5.40
CTAB ^b /TEA ^d (0.017 M) ^c	0.673	0.267	0.053	0.007	0.001	35.0	55.0	10.0
CH ₃ CN/TEA ^d (0.005 M)						26.4	62.5	11.1

^aTetrachlorobenzene isomers ^b0.20 M CTAB ^cRefers to microscopic concentration

^d0.0165 M TEA

Table 9. Tetrachlorobenzene Regioisomer Distribution from Irradiation in Micellar Solution.

Conditions	Relative Percentages		
	<i>para</i>	<i>meta</i>	<i>ortho</i>
This Experiment (with TEA)	31.5	57.5	11.1
$h\nu$, CH ₃ CN ^a 0.011 M ArCl (no CTAB)	38.53	45.95	17.6

^a Reference 9.

time are shown in appendix D.

The significance of the results of this experiment is unclear. The only major difference between this experiment and those reported by reference 36 is that those experiments were degassed of oxygen prior to irradiation. This suggests that oxygen plays a role in neutralizing the effect of the triethylamine. An additional experiment in which the solution is degassed prior to photolysis should show whether this is true or not.

EXPERIMENTAL SECTION.

Purification of Reagents.

1. Pyridine: Reagent grade pyridine was stored over KOH pellets for 5 days. The liquid was then decanted and heated at reflux over BaO for 2 h. under dry Argon, and then fractionally distilled. The fraction boiling at 114-115 °C was collected over BaO and stored overnight. This fraction was redistilled as above, with the constant boiling fraction (114.5-115 °C) collected and stored over BaO.

2. Toluene: Reagent grade (Baker) toluene was washed twice with concentrated sulfuric acid, followed by washing with aqueous NaOH. The toluene was decanted from the aqueous layer and dried over CaCl₂ overnight. It was then fractionally distilled from sodium metal, with the constant boiling fraction collected (b.p. not recorded). Purity was checked by capillary GC, with no impurities detectable.

3. Methanol: Baker "Photrex" Grade methanol was further purified as follows: into a 500 mL 2-neck, round-bottom flask were added 2.6 mg of magnesium shavings, 0.2 g of resublimed I₂ and 50 mL of methanol. This mixture was heated under reflux until the iodine color disappeared and hydrogen gas evolution ceased. Then, 300 mL of methanol was added, heated at reflux for 0.5 h,

and carefully distilled. The first 25 mL was discarded, and further distillate was collected over freshly vacuum-dried 3A molecular sieves.

4. Dimethylsulfoxide (DMSO): Reagent grade DMSO was stored over NaOH pellets for several days, and then fractionally distilled from the NaOH under vacuum (2 mm Hg). The middle fraction was collected (with constant boiling point at 45 °C) and stored over freshly vacuum-dried 3A molecular sieves. Melting point was 18.4 - 18.9 °C (lit: 18.54 °C).⁴⁰

5. Triethylamine: Reagent grade triethylamine (Baker) was stored over KOH pellets for 2 days. To the decanted liquid was added a small amount (approximately 1 cc) of CaH₂, and this was gently heated until hydrogen gas evolution ceased. The liquid was then distilled, with the constant boiling fraction collected (b.p.: 89.5°C; lit: 89.6°C).⁵⁰

6. Pentachlorobenzene: Commercial pentachlorobenzene (Aldrich) was dissolved in boiling 95% ethanol, filtered, and recrystallized overnight. Crystals were collected and air dried. Melting point was determined to be 83.7 - 84.4 °C (lit.: 86 °C).⁵⁰

7. 1,2,4,5-tetrachlorobenzene: Commercial material (Aldrich, 98%) was dissolved in 125 mL 95% ethanol and recrystallized at room temperature, which it did quite readily. Crystals were collected, washed 3 times with cold ethanol, and dried in a vacuum dessicator overnight. This yielded fine, white needlelike

crystals, with a few small, flat platelike crystals (mp 136.2 - 137.0 °C (uncorrected); lit. 139.5 - 140.5 °C⁵⁰).

8. 2,3,5,6-tetrachlorophenol: 2.68 g of commercial material of poor quality (brown powder, Aldrich) was dissolved in 125 mL of hot ligroin and recrystallized in an ice bath for several hours. Crystals were filtered, washed with cold ligroin and air dried. Slightly gray-brown large needlelike crystals (1.97 g) were recovered for use in further synthesis.

9. 1,4-dimethoxybenzene: 5.8 g of commercial material (Aldrich, 98%) was dissolved in 75 mL of hot 95% ethanol, and recrystallized at room temperature. Crystals collected by filtration were washed with cold ethanol and dried overnight in a vacuum dessicator. Large, platelike, opalescent crystals (1.3 g) were recovered, with mp = 53.9 - 54.6 °C (lit.: 57.2 - 57.8 °C).⁵³

Preparation of 2-methoxy-1,3,4,5-tetrachlorobenzene.

To a 20×150 mm test tube were added 7 mL of 50% aqueous KOH and 15 mL of ether. This was immersed in an ice-water bath, and stirred using a magnetic micro-stir bar. To this tube was carefully added 0.45 g N-nitrosomethylurea over about a 1 h period. Evolution of fine gas bubbles was noted. When the solid urea was completely reacted, the yellow ether layer containing the resultant diazomethane was pipetted to a test tube in an ice-water bath, and several KOH pellets were added to remove trace water. This diazomethane solution was added

dropwise to a chilled solution of 0.41 g of 1,3,4,5-tetrachlorophenol in 5 mL of ether, and the solution was periodically swirled, until the mixture retained the yellow diazomethane color and gas evolution ceased. The excess diazomethane and ether were allowed to evaporate, and a yellow-pink-white fluffy crystal resulted. This was recrystallized from methanol, yielding a fluffy white crystal (m.p. 50-54 °C). Overall yield 68%. Analysis: ^1H NMR: δ =3.908 (3H, s); 7.46 (1H, s); impurity showed peaks at δ =1.55 (s) and 3.917 (s). GC: Capillary GC (Varian 3400) with DB225 column shows two peaks at t_{ret} =22.14 and 27.47 min corresponding to the desired product and impurity, with relative intensities, respectively, 84.8% and 10.7%. The impurity peak does not correspond to the starting material (t_{ret} =29.48 min).

Preparation of 1-methoxy-2,3,5,6-tetrachlorobenzene.

Prepared from the corresponding phenol using the same procedure as above. Crude product was dissolved in hot water to remove unreacted urea, and crystals were recrystallized from methanol/water. Yielded white, needlelike crystals with mp = 87.5 - 88.0° C (uncorrected)(lit.: 89 - 90 °C).⁵⁰ Greater than 99% pure by GC (no impurities detected).

Preparation of 2,3,5,6-tetrachlorophenylhydrazine (2).³⁸

A modification of the procedure reported by N. J. Leonard was used.⁵¹ To

a 50 mL Bantamware three-necked roundbottom flask equipped with a dropping funnel, thermometer and condenser, under dry Argon atmosphere, was added 30 mL of 95% ethanol. The flask was then heated to reflux in an oil bath. Reagent grade 2,3,5,6-tetrachloronitrobenzene (10 g, 0.038 mol) was added and the solution was magnetically stirred. Hydrazine hydrate (10 g) was slowly dropped in. A white precipitate formed immediately and then dissolved. After a few minutes a copious amount of solid formed. The mass was heated at reflux for a total of two hours and then transferred to a beaker, and 50 mL of 7% aqueous KOH was added. This mixture was stirred for one hour to ensure that all triazoline (approximately 6% reported) was extracted. The remaining solid was isolated by vacuum filtration, washed twice with 25 mL portions of water, and recrystallized from ethanol to give 4.5 g (0.018, 48% yield) of pure white crystalline hydrazine (2). Analysis: ^1H NMR (300MHz, CDCl_3) δ 4.00(d, 2H, $J=1\text{Hz}$, $-\text{NH}_2$), 5.75(br s, 1H, $-\text{N}'\text{H}$), 7.29(s, 1H); High resolution mass spectrometry: best correlation had -0.2 ppm mass deviation from 243.91280 with formula $\text{C}_6\text{H}_4\text{N}_2\text{Cl}_4$.

Preparation of N-(2,3,5,6-tetrachlorophenyl)-N'-trityl-hydrazine (3)³⁸

A modification of the procedure reported by Cohen for N-phenyl-N'-tritylhydrazine was used.³⁷ To a 500 mL three-necked roundbottom flask equipped with a mechanical stirrer, condenser, argon inlet and thermometer was added 300 mL of freshly distilled THF. Trityl chloride (11.25 g, 0.040 mol) was added. The solution was heated to 65 °C. Hydrazine (2) (20 g, 0.080 mol)

was then added in one portion. A solid immediately formed after dissolution of the hydrazine, and the mixture was heated at reflux for 3 hours. Upon cooling, the mixture was vacuum filtered and the solid discarded. Evaporation of solvent from the remaining solute gave 19.6 g of crude product. Recrystallization from a minimum amount of acetone gave 12.0 g (0.025 mol, 31% yield) of white crystalline hydrazine (3). Analysis: ^1H NMR(300MHz, CDCl_3) δ 4.73 (s, 1H), 5.40 (s, 1H), 7.2-7.5 (m, 15H); High resolution mass spectrometry: best correlation had 0.4 ppm deviation from mass 486.02260 with formula $\text{C}_{25}\text{H}_{18}\text{N}_2\text{Cl}_4$.

Preparation of 2,3,5,6-tetrachlorobenzene-azo-triphenyl-methane (TCBAT)(4).³⁸

A modification of a procedure reported by Dimroth was used⁵². To a 500 mL three-necked Morton flask equipped with a high-speed stirrer and condenser, under Argon atmosphere, were added 200 mL of CH_2Cl_2 (spectro quality), 48 mg (0.149 mmol) of 2,4,6-triphenylphenol and 200 mL of 2N aqueous NaOH saturated with $\text{K}_3\text{Fe}(\text{CN})_6$ (70 g of $\text{K}_3\text{Fe}(\text{CN})_6$ per 200 mL of 2N NaOH). Hydrazine (3) was then added in one portion. The organic phase was isolated and the remaining aqueous phase extracted once with CH_2Cl_2 . The combined organic layers were washed three times with water and filtered through a small amount of silica gel to remove any remaining phenoxide, and then dried over Na_2SO_4 . Careful evaporation of solvent gave 3.34 g (7.9 mmol) of crude product. Recrystallization of 0.54 g from methanol gave 0.39 g (69% yield) of finely divided orange crystalline product (mp xxxx). Analysis: ^1H NMR (300MHz, CDCl_3) δ 7.2-7.4 (m,

15H), 7.54 (s, 1H); Mass spectrometry: using M + H peak, best correlation was -.28 ppm deviation from mass 485.01430 with formula $C_{25}H_{17}N_2Cl_4$ (giving M^+ of $C_{25}H_{16}N_2Cl_4$).

Preparation of 1.0 M Methanolic Sodium Methoxide Solutions.

Metallic sodium was pared of the oxide layer and weighed under xylene, and 1.4 g (5.9×10^{-2} mol) was cleaned by immersion in methanol and dissolved in 50.0 mL anhydrous methanol. This solution was standardized by titration with 0.459 N HCl using phenolphthalein indicator, and found to be 0.995 M. The liquid was decanted from the small amount of solid formed, and the solution was stored under dry Argon.

Kinetics of the Thermal Methoxydechlorination of Pentachlorobenzene in Pyridine.

To a 3-necked, roundbottom flask fitted with an argon purge line and a rubber septum for sampling were added 0.680 g (2.72×10^{-3} mol) of pentachlorobenzene, 0.415 g (3.01×10^{-3} mol) of 1,4-dimethoxybenzene (internal standard), and a magnetic stirring bar. Pyridine (22.3 mL) and 2.73 mL of 0.995 M (2.72×10^{-3} mol) methanolic sodium methoxide were added under a argon purge, and the solids were dissolved. After an initial sample (about 0.5 mL) was syringed out, the mixture was heated in an oil bath to 93 ± 1 °C. Small samples were taken at various times and quenched with a drop of glacial acetic acid. Samples were

analyzed by GLC on a Hewlett-Packard F & M 700 gas chromatograph equipped with a 0.25 in \times 10 ft copper tubing column packed with 4.1% Carbowax 20M on Chromosorb W AW DMCS (80/100 mesh), a thermal conductivity detector, and a SpectraPhysics 4290 integrator. Conditions were: injector temperature 270 °C, column temperature 175 °C, detector temperature 285 °C, column gas (He) flow rate 60 mL/min, and reference gas flow rate 5 mL/min.

It should be noted that during the reaction, the color of the solution went from colorless and clear, through yellow, brown and finally red-brown. These colors changed to varying intensities of violet-purple on addition of acid. It was not determined what caused these color changes.

Kinetics of the Thermal Methoxydechlorination of Pentachlorobenzene in Dimethylsulfoxide.

1. General Procedure: Reaction vessels were heated in an oil bath maintained at $50 \pm 0.1^\circ\text{C}$ using a proportional temperature controller with a platinum thermistor probe (Cole-Parmer model 2156-00 controller/ YSI series 400 probe), a 450 W blade-type immersion heater (CSC model 16651-003) and a motor-driven stirring blade. Pentachlorobenzene and 1,4-dimethoxybenzene (internal standard) were weighed into the reaction vessel (a 50 mL 3-necked, roundbottom flask or a 50 mL, 2-necked, cylindrical flask), and DMSO and methanol were added to make the solution approximately 0.01 M in pentachlorobenzene. Depending on the reaction conditions, solutions were degassed by either the vacuum freeze-thaw method or by bubbling dry Argon into

solution via a gas dispersion tube, saturated with oxygen by bubbling compressed air into solution, or no treatment was done at all. Experiments involving radical traps added 3 - 7 mol% of galvinoxyl (Aldrich, used as received). The reaction vessel was fitted with a gas purge line to maintain positive gas pressure during the reaction, and a rubber septum to facilitate sample transfer via syringe. This mixture was heated in the oil bath until temperature stabilized. After taking a 0.5 mL sample via syringe for time $t = 0$, 1.00 M methanolic sodium methoxide (prepared from methanol and sodium metal, and standardized by titration with aqueous HCl and phenolphthalein indicator) was added via Eppendorf pipette to give equimolar amounts of methoxide and pentachlorobenzene in the reaction mixture. Reaction time was measured with a stopwatch, and 0.5 mL samples were taken periodically via syringe.

2. Sample Extraction and Analysis: Each sample was immediately transferred to a 2 mL sample vial containing about 0.3 mL of toluene and one drop of glacial acetic acid, which quenched the reaction. After mixing, 1 mL of distilled water was added, and the vial was capped and shaken. (This technique was shown to give a highly quantitative extraction of test mixtures). The toluene layer was analyzed by GLC on a Varian 3300 capillary gas chromatograph equipped with a flame-ionization detector, a $30\text{ m} \times 0.25\text{ mm}$ DB-WAX (J & W Scientific, Inc.) or DB-225-II (Econocap) capillary column, and a SpectraPhysics 4290 integrator. The column was held at $150\text{ }^{\circ}\text{C}$ for 5 min and raised to $200\text{ }^{\circ}\text{C}$ at a rate of $5\text{ }^{\circ}\text{C}/\text{min}$, with an injection port temperature of $300\text{ }^{\circ}\text{C}$ and a detector temperature of $350\text{ }^{\circ}\text{C}$. Helium was used as carrier gas at $30\text{ mL}/\text{min}$. Peak areas were corrected

using previously determined response factors. Selected samples were further analyzed by GC-mass spectrometry. For some samples, the *para*- and *meta*-tetrachloroanisoles (which were unresolvable by GC) were isolated by preparative gas chromatography (Hewlett-Packard F & M 700 GC equipped with a 0.25" \times 10' packed column containing SE-30 liquid phase on Anakrom 80/100 mesh) and further analyzed by proton NMR. The aromatic ring proton signal integrated area was used to determine relative amounts of these isomers present.

Thermal Methoxydechlorination of Tetrachloroanisoles in DMSO and Product Study.

Small amounts (20 to 30 μ mol) of tetrachloroanisole were added to reaction tubes, with one isomer per tube. To each tube was then added 3.00 mL of a solution made up by mixing 10.0 mL of DMSO, 0.56 mL of methanol and 0.12 mL of 1.09 M methanolic sodium methoxide. Tubes were capped with a rubber septum, and placed in a 50.0 ± 0.1 °C oil bath for 45 minutes. The mixtures were quenched with acetic acid, extracted and analyzed by GC as in the kinetics experiments described above. These extracts were submitted for GC-MS analysis to the OSU Low Resolution GC-MS Facility.

Test of the Thermal Stability of *para*-dimethoxybenzene.

To a sealable pyrex tube were added 0.0199 g (1.44×10^{-4} mol) of the dimethoxybenzene, 3.0 mL of DMSO and 0.1 mL of 1.0 M (1.0×10^{-4} mol)

methanolic sodium methoxide. The tube was capped and heated to 50 °C for 70 min. The reacted mixture was extracted and analyzed by GC as described above. No peaks other than solvent and starting material were detected.

Experimental Test for a Benzyne Mechanism in the Methoxydechlorination Reaction.

A mixture of 10.0 mL of DMSO, 0.556 mL methanol, 0.0421 g (1.68×10^{-4} mol) of pentachlorobenzene, 0.0206 g (1.49×10^{-4} mol) p-dimethoxybenzene, and 0.0577 mL of 1.09 M methanolic sodium methoxide was prepared, and 4.0 mL of this solution was added to each of two sealable tubes. To one of the tubes was added 0.0065 g (2.40×10^{-5} mol) of 1,3-diphenylisobenzofuran (Aldrich, used as received). The tubes were capped and heated in a 50 ± 0.1 °C oil bath for 20 min and extracted and analyzed by capillary GC by methods described earlier.

Photodechlorination of Pentachlorobenzene in Aqueous Micellar Solution.

1. Preparation of micelle solution: Cetyltrimethylammonium bromide (CTAB) (Aldrich) was purified by recrystallization from ethanol and washed with hexane. Water was purified by distilling deionized water from potassium permanganate (bp = 100.0 °C). Cetyltrimethylammonium bromide (14.57 g, 0.03998 mol) was dissolved in about 175 mL of water in a 200 mL volumetric flask with stirring and gentle heating. Once dissolved, water was added to make

200 mL of 0.200 M aqueous CTAB solution.

2. General reaction and analysis procedure: in a cylindrical pyrex reaction vessel (4" long, 1.25" diameter, with two ground glass joints on top) was added 0.0130 g (5.20×10^{-5} mol) of pentachlorobenzene and 50.0 mL of 0.200 M CTAB and stirred until dissolution was achieved. In reactions using triethylamine, 1.15 mL (8.27×10^{-3} mol, where a density of 0.7275 g/mL was assumed⁵⁰) of triethylamine was added just prior to photolysis. The vessel was placed approximately 10 cm from a General Electric sunlamp, with continuous magnetic stirring. Periodic samples (1.0 mL) were taken by syringe. Samples were extracted 3 times with 200-300 mL of water, 20 mL of brine, 10 mL of 2 N aqueous HCl and 30 of mL pentane. The pentane extract was condensed by rotary evaporation to dryness, and redissolved with 0.1 mL hexane containing 0.033 M dodecane as internal standard. Samples were analyzed by capillary GC (Varian 3400 equipped with a 30 m DB-WAX column) using a temperature program 60 - 180 °C, 5 min initial hold, 5°C/min heatup rate, with injector temperature 250 °C and detector temperature 300 °C. Response factors for penta-, tetra-, tri- and di-chlorobenzenes were determined relative to dodecane using authentic standards. GC-MS was used to identify peaks which did not correspond to compounds with known retention times.

**Competitive Kinetic Studies of Thermally Generated
Tetrachlorophenyl Radicals.**

A procedure similar to that reported by Bridger and Russell²⁶ was used. Solutions of 0.1 M of 2,3,5,6-tetrachlorobenzeneazotriphenylmethane (TCBAT) were prepared in solvent mixtures containing carbon tetrachloride (Baker, HPLC grade) and one of the following: triethylamine, diazabicyclo[2.2.2]octane (DABCO), quinuclidine or *d*₃-acetonitrile (Aldrich, 100 %d). Small portions (0.500 mL) were transferred to 2 mL ampoules. These were degassed by three freeze-pump-thaw cycles, and sealed under vacuum. These ampoules were heated to 60 ± 0.1 °C for four hours in an oil bath, and were kept in a freezer until analyzed. Analysis was done by GC on a Varian 3300 capillary GC equipped with a 30 m DB WAX column. The temperature program was the same as used in the previous experiment (photodechlorination in micelles).

Determination of Rate of Decomposition of TCBAT.

Ampoules containing 0.500 mL of a 0.1 M solution of TCBAT in carbon tetrachloride were prepared as in the competitive rate experiments above. These ampoules were placed in a 60.0 or 75.0 ± 0.1 °C oil bath. An ampoule was removed periodically, opened and diluted with 3.0 mL of hexane.

Ultraviolet/visible spectra were taken of these diluted samples using a Hewlett-Packard 8452A UV/VIS Diode Array Spectrophotometer. The instrument was calibrated to a blank solution containing 0.500 mL CCl₄ and 3.0 mL hexane. The absorbance at $\lambda = 450$ nm was used to calculate concentration of each sample, since no interference from product absorption occurred at this wavelength. A kinetic plot of the logarithm of relative concentration (i.e., absorbance at time *t*

divided by absorbance of the unreacted sample) versus time was generated using this data, and decomposition half-lives were measured directly from these plots.

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APPENDICES

APPENDIX A

Rate Expression for Second-Order Kinetics

The second-order rate expression used for kinetic studies of the methoxydechlorination reaction of pentachlorobenzene is derived.

Let:

$[\text{PCB}]_t$ = *actual* pentachlorobenzene concentration in the
reaction mixture at time t

$[\text{STD}]$ = *actual* concentration of internal standard
(*para*-dichlorobenzene) in reaction mixture
(constant)

$(\text{pcb/std})_t$ = GC integrated peak area ratio of pentachlorobenzene
to internal standard at time t

R = response factor of the GC detector to pentachlorobenzene
and standard, i.e., $[\text{PCB}]_t/[\text{STD}] = R(\text{pcb/std})_t$. In
practice, R is calculated by measuring the initial
PCB/STD GC area ratio $(\text{pcb/std})_{t=0}$ and comparing
the known actual initial concentration ratio of the
two.

Now, using the general expression for second order kinetics^{ref} in the case where the two reactants start in equal concentrations:

$$kt = 1/a_t - 1/a_0$$

where a_t and a_0 are the concentrations of the reactant at time t and initially.
In terms of this experiment:

$$kt = 1/[\text{PCB}]_t - 1/[\text{PCB}]_0.$$

A numerical value for $[\text{PCB}]_t$ can be obtained from the integrated GC areas by the relation given above in the definition for R . Rearranged a bit, this expression for R becomes:

$$[\text{PCB}]_t = R[\text{STD}](\text{pcb/std})_t.$$

Using this expression in the kt equation gives:

$$\begin{aligned}
 kt &= \frac{1}{R[\text{STD}](\text{pcb}/\text{std})_t} - \frac{1}{[\text{PCB}]_0} \\
 &= \frac{1}{R[\text{STD}]} \left(\frac{\text{std}}{\text{pcb}} \right)_t - \frac{1}{[\text{PCB}]_0}
 \end{aligned}$$

Multiplying by $R[\text{STD}]/R[\text{STD}]$, and then factoring out $1/R[\text{STD}]$ gives:

$$kt = \frac{1}{R[\text{STD}]} \left\{ \left(\frac{\text{std}}{\text{pcb}} \right)_t - \frac{R[\text{STD}]}{[\text{PCB}]_0} \right\}$$

Once again using the defining expression for R , and rearranging, the second term in brackets $\{ \}$ in the last equation becomes:

$$R[\text{STD}]/[\text{PCB}]_0 = (\text{std}/\text{pcb})_0$$

the right-hand side of which is directly measurable by GC. So, the expression for kt now becomes:

$$kt = \frac{1}{R[STD]} \left\{ \left(\frac{\text{std}}{\text{pcb}} \right)_t - \left(\frac{\text{std}}{\text{pcb}} \right)_0 \right\}$$

This expression is now in terms of measurable quantities. The kinetic plots of each experiment was done by plotting the kt from this equation versus time. Thus, the value of k can be deduced directly from the slope of a linear plot if the reaction is indeed second-order.

APPENDIX B

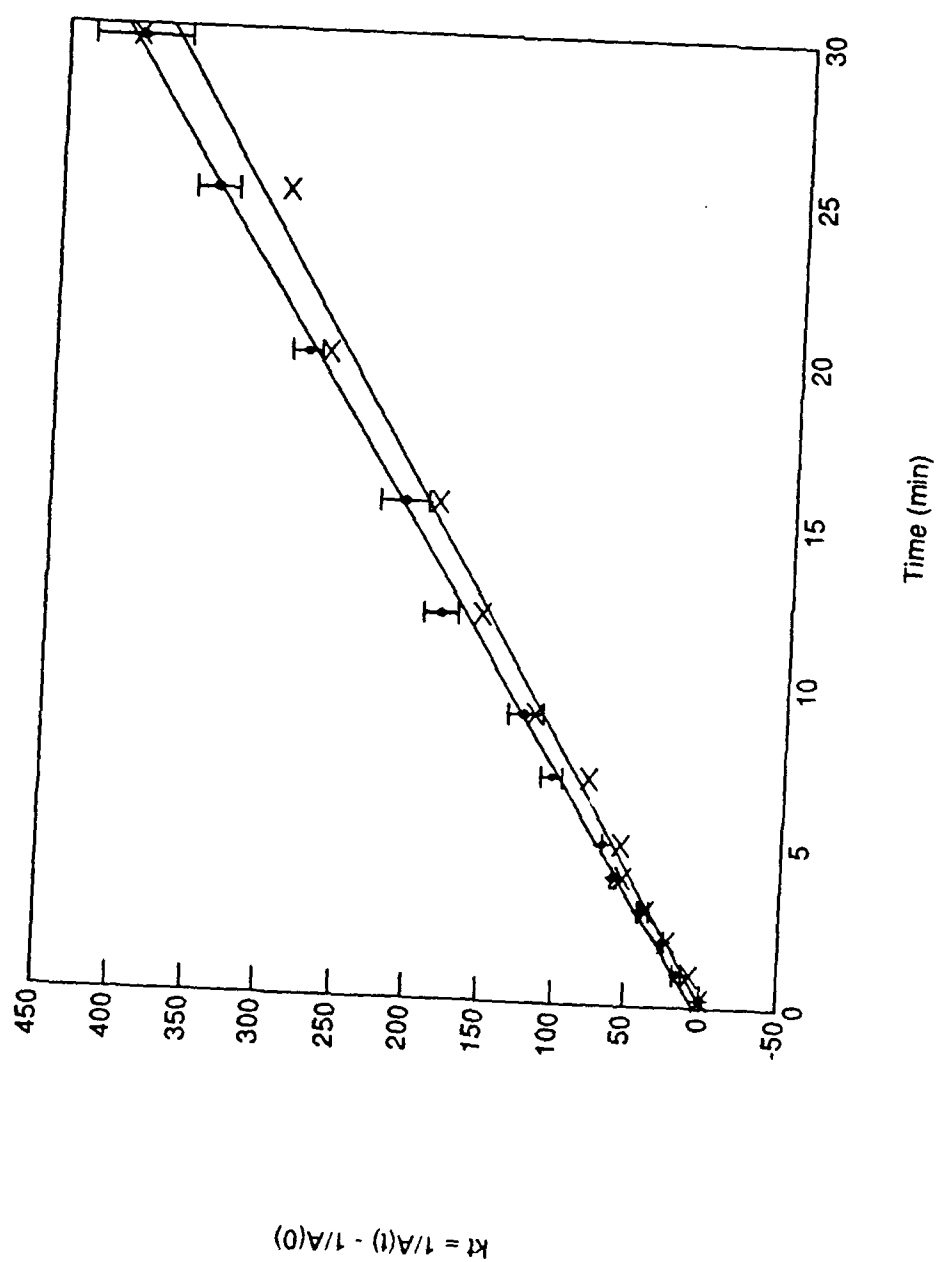


Figure B-1. Second-order kinetic plots of pentachlorobenzene methoxydechlorination in DMSO:methanol (13.9:1 v/v) at 50 °C with (lower curve) and without (upper curve) galvinoxyl.

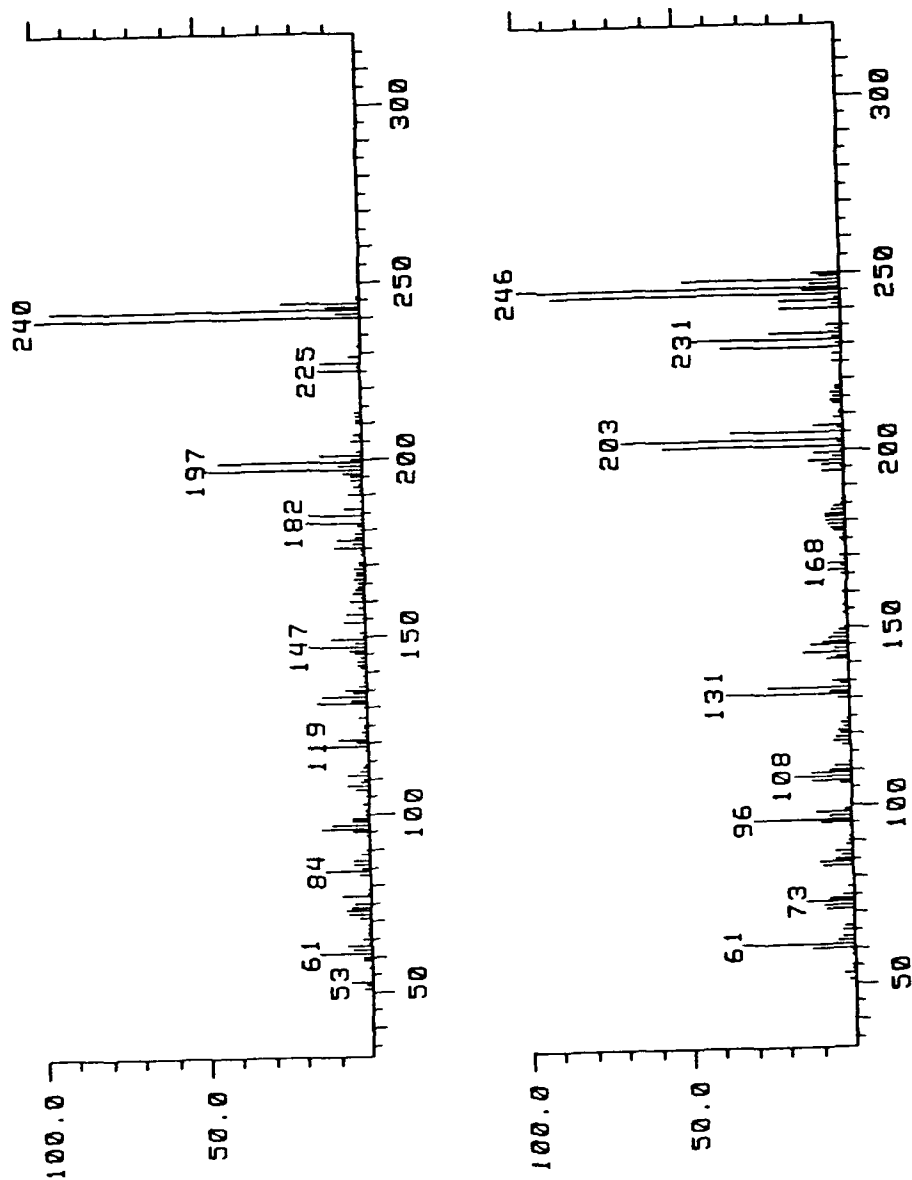


Figure B-2. GC-MS spectra of an isomer of trichlorodimethoxybenzene (TDB, top) and of the *ortho*-tetrachloroanisole GC peak which contains approximately 10% TDB.

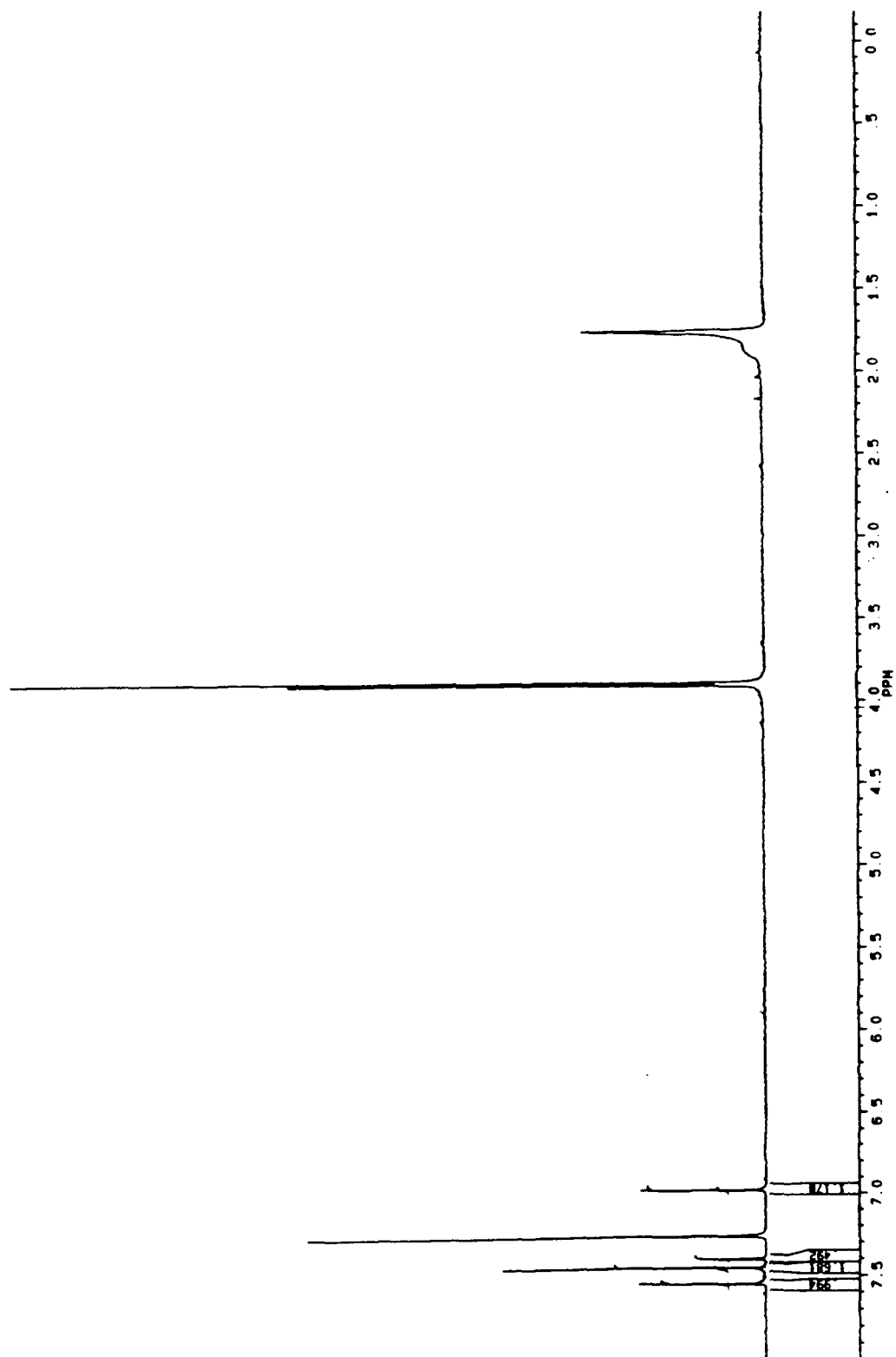


Figure B-3. 300 MHz proton NMR spectrum of a mixture of pentachlorobenzene and 3-tetrachloroanisole isomers (in CDCl₃).

APPENDIX C

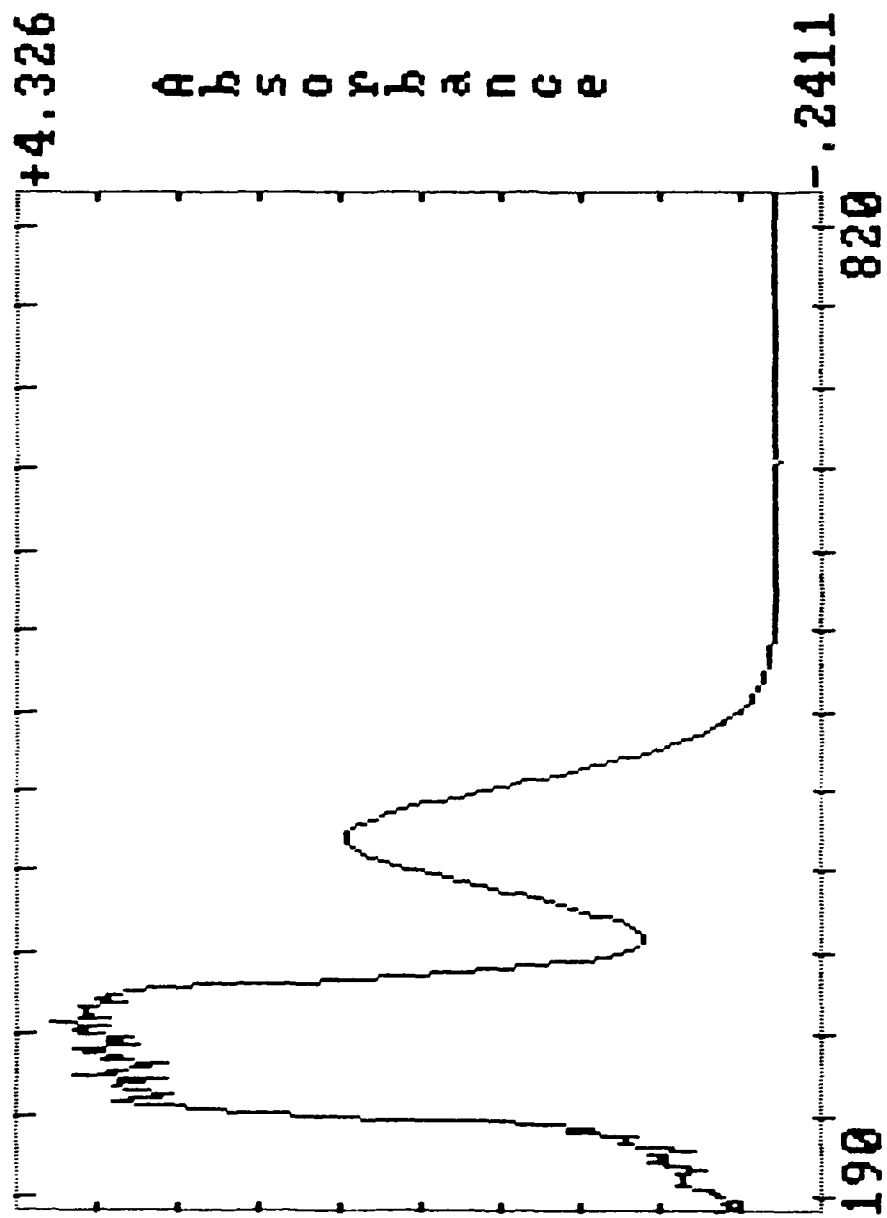


Figure C-1. UV/VIS spectrum of 1,2,4,5-tetrachlorobenzeneazotriphenylmethane.

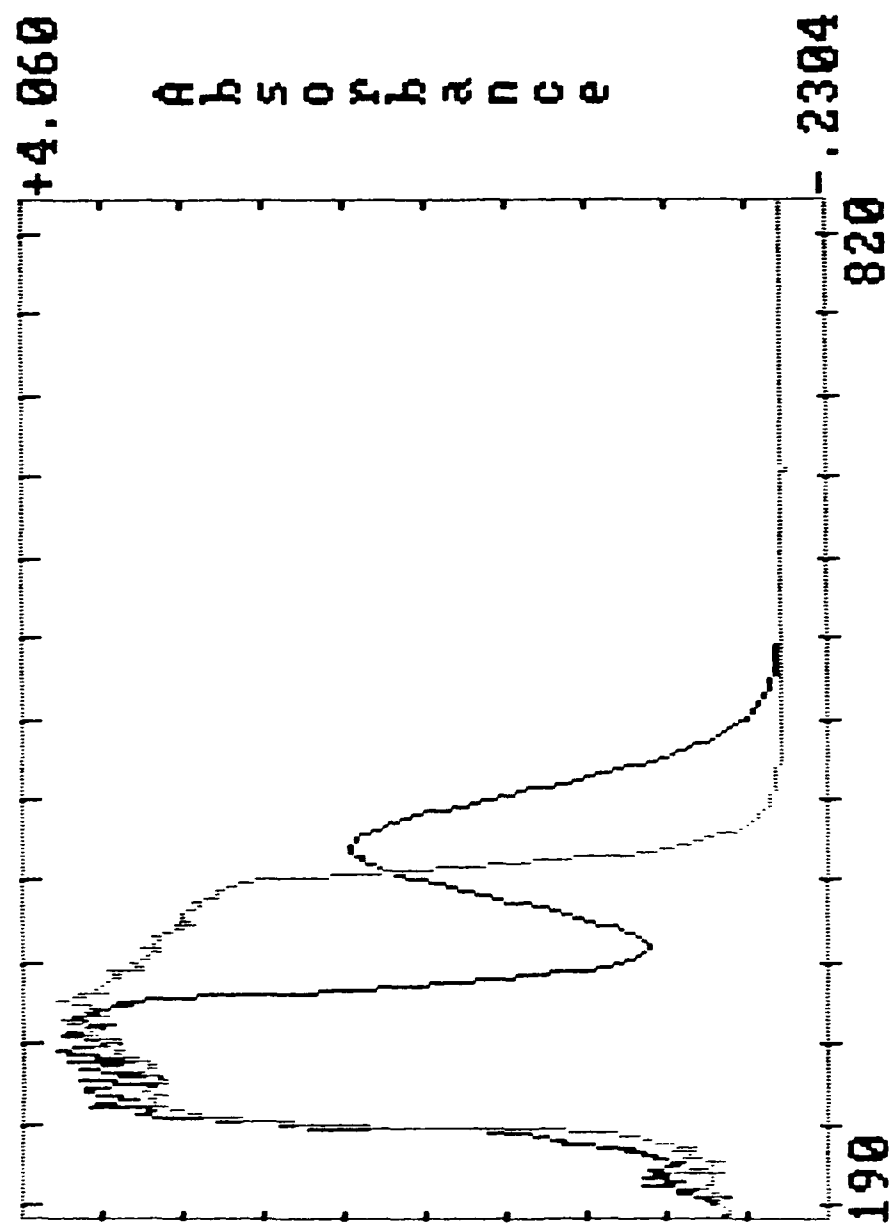


Figure C-2. UV/VIS spectrum of unreacted (dark line) and completely reacted (light line) 1,2,4,5-tetrachlorobenzencazotriphenylmethane in CCl_4 .

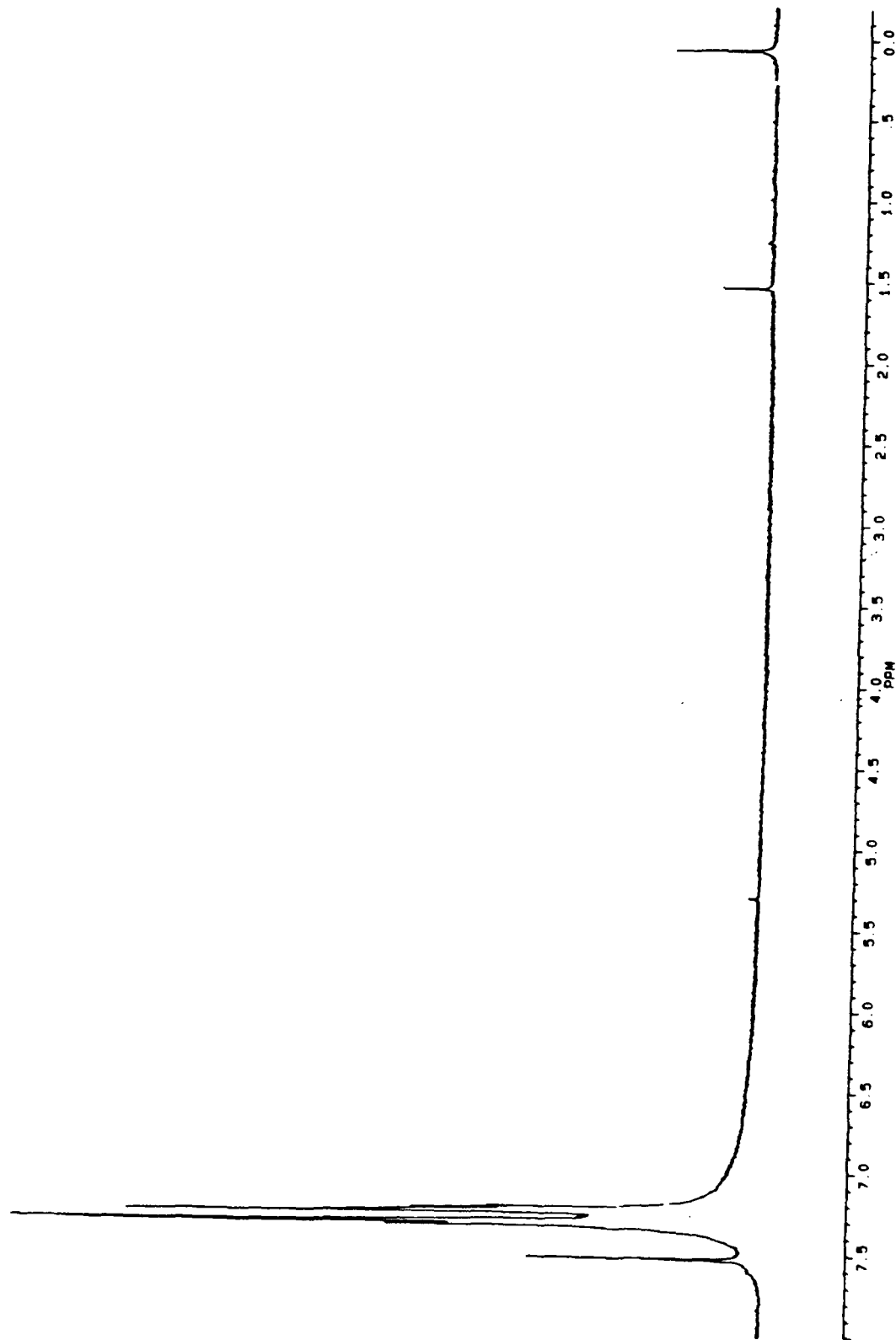


Figure C-3. 300 MHz proton NMR spectrum of 1,2,4,5-tetrachlorobenzeneazotriphenylmethane (in CDCl_3/TMS).

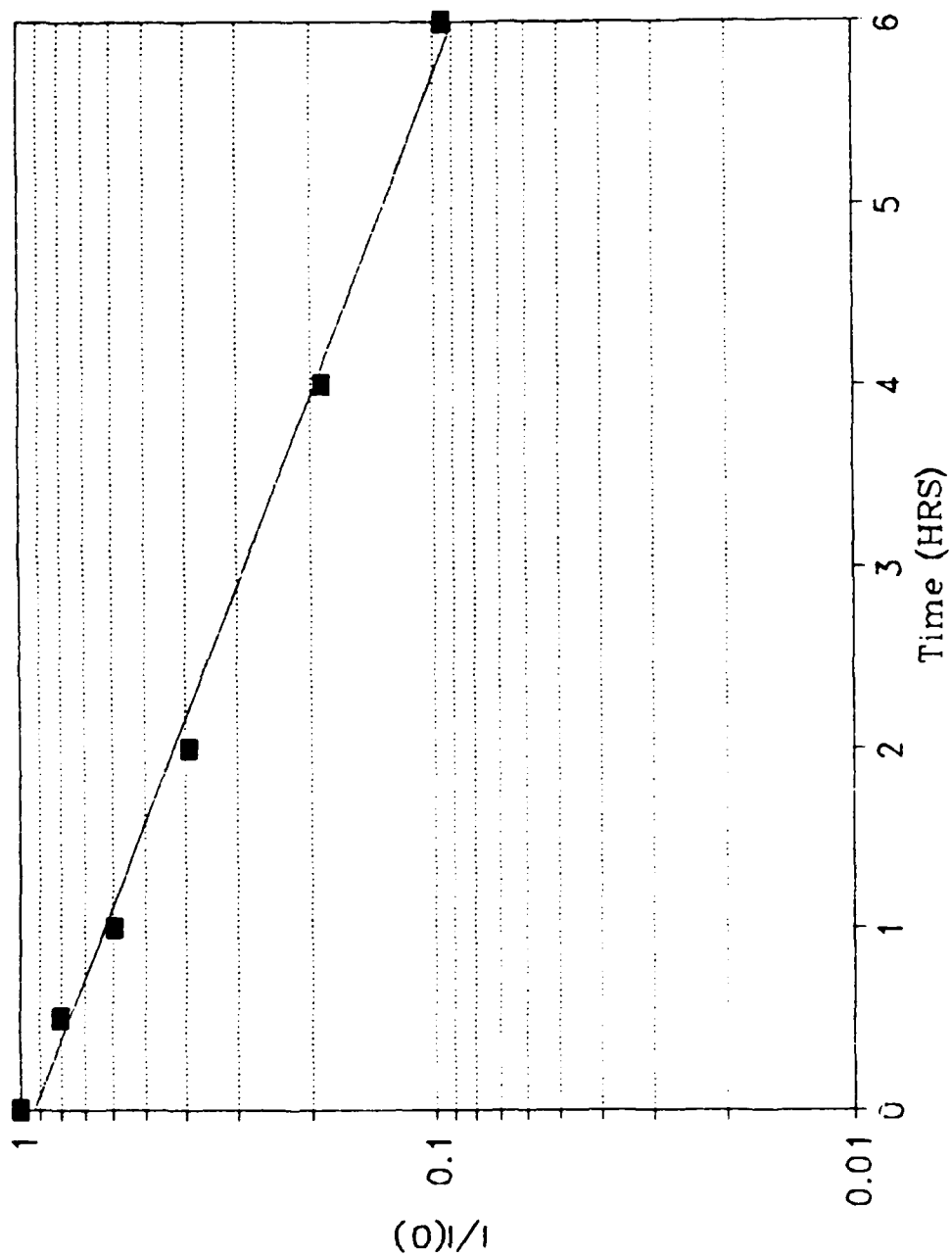


Figure C-4. First-order kinetic plot of the rate of decomposition of TCBAT at 60.0 °C in CCl₄.

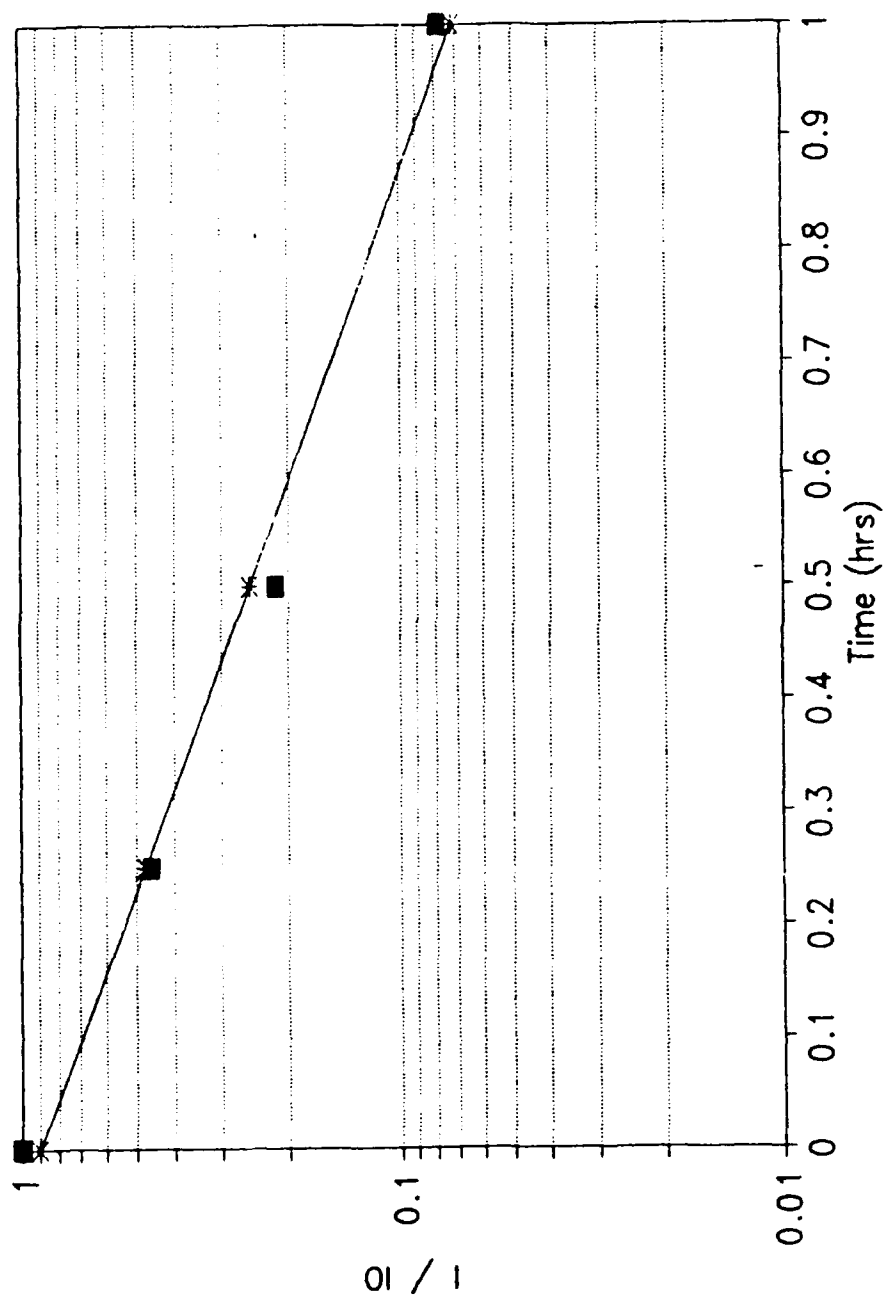


Figure C-5. First-order Kinetic Plot of the Rate of Decomposition of TCBA at 75.0 °C in CCl₄.

APPENDIX D

$\langle S \rangle \longrightarrow$	0.396	0.527	0.659	1.32	1.68	1.82	2.08	2.60	3.52
P(0)	0.673	0.590	0.517	0.267	0.186	0.162	0.125	0.074	0.030
P(1)	0.267	0.311	0.341	0.353	0.313	0.295	0.260	0.193	0.104
P(2)	0.053	0.082	0.112	0.233	0.263	0.268	0.270	0.251	0.183
P(3)	0.007	0.014	0.025	0.102	0.147	0.163	0.187	0.218	0.215
P(4)	0.001	0.002	0.004	0.034	0.062	0.074	0.097	0.141	0.189
P(5)	0.000	0.000	0.001	0.009	0.021	0.027	0.041	0.074	0.133
P(6)	0.000	0.000	0.000	0.002	0.006	0.008	0.014	0.032	0.078
P(7)	0.000	0.000	0.000	0.000	0.001	0.002	0.004	0.012	0.039
P(8)	0.000	0.000	0.000	0.000	0.000	0.000	0.001	0.004	0.017
P(9)	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.001	0.007
P(10)	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.002

Table D-1. Numerical Solutions to Poisson Distribution at Various Values of $\langle S \rangle$.

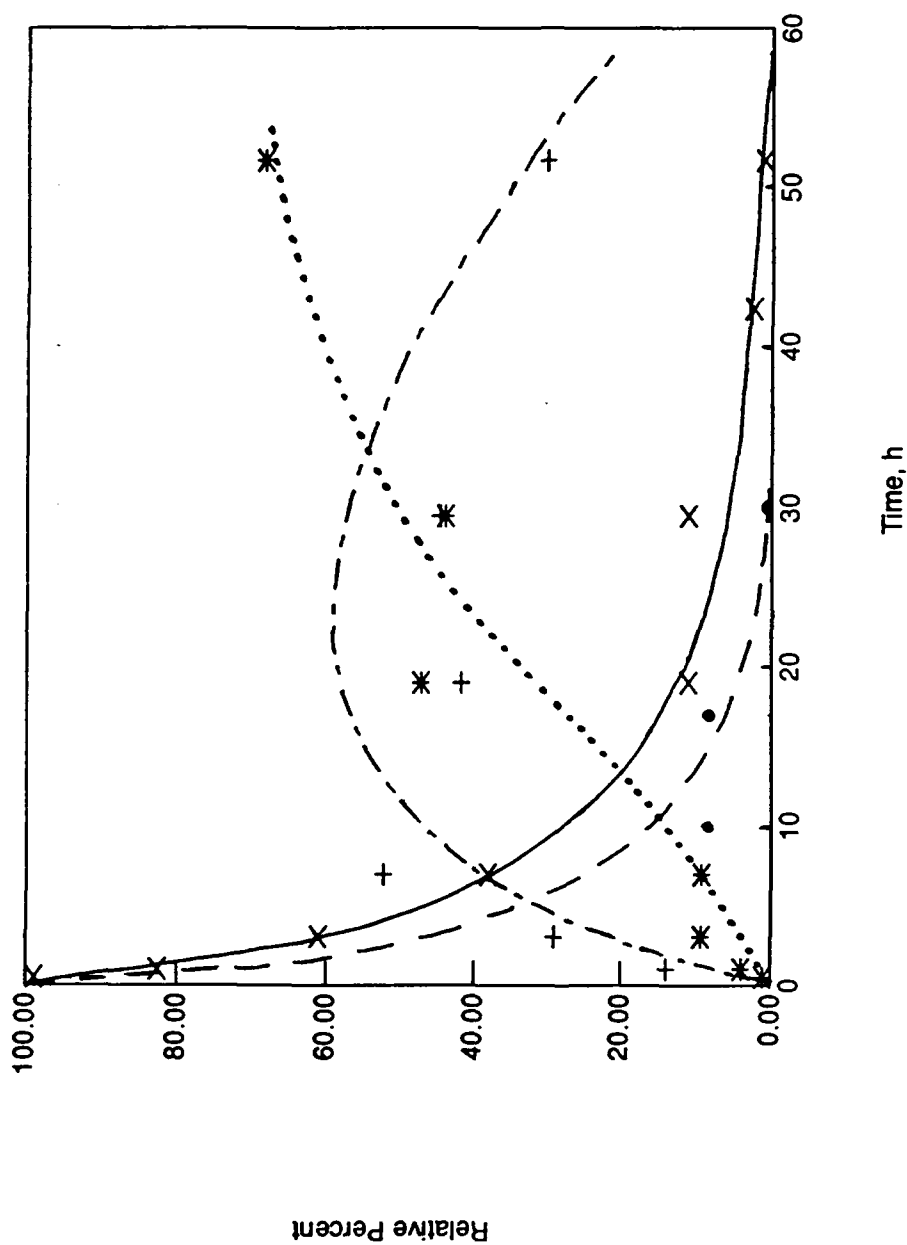


Figure D-1. Plot of relative concentrations of pentachlorobenzene (—), tetrachlorobenzenes (— · — · —), and trichlorobenzenes (•••••) versus time during irradiation in micellar solution in the presence of triethylamine, and pentachlorobenzene relative concentration versus time in reactions without triethylamine (— — —).